NITRATE REMOVAL FROM WATER
BY
BISMUTH-BASED MEDIA

A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY
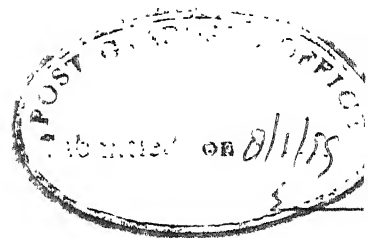
by

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January, 1999

CERTIFICATE

Certified that the work presented in this thesis entitled NITRATE REMOVAL FROM WATER BY BISMUTH-BASED MEDIA by Prabhat Kumar Singh has been carried out under my supervision and has not been submitted elsewhere for a degree.

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ABSTRACT

With a view to develop an inorganic medium for nitrate removal from water, bismuth compounds in the form of oxide, oxychloride, carbonate and hydroxide were subjected to short duration (3h) batch screening tests to assess their potentials and identify the most promising compound. These tests indicated that bismuth hydroxide in its yellow colored composition gives best performance in terms of nitrate removal. Observations revealed that preparative conditions of bismuth hydroxide had significant effects on its physicochemical properties.

Three hydrous bismuth oxides (HBOs), designated as HBO (1), HBO (2) and HBO (3), prepared from a 0.1M Bi_2O_3 solution in 2N HCl with increasing volumetric proportions of 1:1, 1:2, and 1:3 of 2N NaOH respectively, had differing physical as well as nitrate removal properties. HBO (1) was visibly white in color and showed a poor nitrate removal. HBO (2) and HBO (3), on the other hand, were predominently yellow and displayed high nitrate removals. In batch sorption tests (initial nitrate concentration: I meq/L, powder dosage: 40 g/L; contact time: 24h), HBO (1), HBO (2), and HBO (3) showed 16.0, 81.6 and 81.7% nitrate removals respectively. Tests for kinetics of removal by yellow colored HBO (2) and HBO (3) indicates that most of the sorption takes place within initial 2h of contact.

Nitrate sorption (removal) experiments indicated exchange of chloride from HBO (2) and HBO (3). Based on observations (this study) and the literature report that the physical characteristics and chemical composition of metal

hydroxide precipitate are significantly affected by the anions in the aquous medium, presence of chloride in HBOs was investigated. Mass balance of chloride indicated that HBO (1), HBO (2) and HBO (3) had a chloride content of 280, 110 and 40 mg/g respectively. Investigations about the mode of existence of chloride in hydrous bismuth oxides revealed that the ions are retained within the precipitate by rather "weak interactions".

Sorption equilibria for nitrate on HBO (2) and HBO (3) indicated exchange of chloride. Chloride Exchange Ratio (the ratio of amount of chloride released (meq/g) to the amount of nitrate sorbed (meq/g)), for HBO (2) and HBO (3) were estimated as 0.75 – 0.85 and 0.65 – 0.79 respectively. In column tests (influent: I meq/L nitrate in distilled water; medium: wet volume. 8.35 mL for HBO (2) and 7.35 mL for HBO (3); and flow = 1.10-2.00 mL/min), chloride exchange ratio of 0.96 and 0.85 were observed for HBO (2) and HBO (3) respectively. pH of effluents from both of HBO (2) and HBO (3) columns ranged between 7.0 and 8.0 indicating that OH$^-$ ions are not the counter ion of exchange for nitrate sorption.

Tests to understand the regeneration and reuse potentials of HBO (2) and HBO (3) indicated that while sodium hydroxide solution eluted the sorbed nitrate, it could not regenerate the media for further use. Sodium chloride solution could elute the sorbed nitrate and regenerate the media for successive use. During regeneration, a recovery ratio (the ratio of nitrate eluted during regeneration to nitrate sorbed before regeneration) of 0.60 and 0.49 was observed for HBO (2) and HBO (3) respectively. This indicates HBO (2) to be better ion exchanger than HBO (3) for nitrate removal from water. In each cycle of operation (medium; 10g: influent: I meq/L nitrate in distilled water) and regeneration (regenerant: 0.1N

sodium chloride), around one liter of water having less than 10 mg N/L was produced by HBO(2).

Tests for the behavior of competitive anions such as bicarbonate and sulfate indicated that these ions are also sorbed with chloride exchange. Nitrate removal decreased in presence of these ions HBO (2) showed a preference of ion sorption as

$$HCO_3^- > SO_4^{--} > NO_3^-$$

Performance evaluation of HBO(2) powder in nitrate removal from ground water spiked with 1 and 2 meq/L of nitrate also indicated its effectiveness However, due to higher preference for bicarbonate, nitrate as well as sulfate "dumping" were observed. Regeneration of used medium by sodium chloride solution indicated elution of sorbed nitrate, alkalinity and sulfate These results, thus show that hydrous bismuth oxides have definite potentials for nitrate removal from water and regeneration of the media by sodium chloride solution make their use simple. A pretreatment of ground and surface waters for decreasing the levels of alkalinity and sulfate appears desirable before an effective use of these media for nitrate removal in water treatment applications.

Dedicated to

Lord Shri Krishna

Through

My Spiritual Master

H.H. Bhaktisvarupa Damodara Swami Sripada

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CHAPTER 1

INTRODUCTION

Nitrate concentration levels are increasing in surface as well as ground waters. Nitrate is the most ubiquitous chemical contaminant in the world's aquifer and the levels of contamination are reported to be increasing worldwide. Around 90% of the population in India is dependent on ground water as the only source of drinking water. Alarming nitrate concentration levels have been reported in ground waters from several districts of Haryana, Punjab, Rajasthan, Gujrat, Uttar Pradesh, Bihar, West Bengal and many other states. In farmed areas ground water nitrate contamination mainly originates from the excessive application of nitrogenous fertilizers. Nitrates may also be contributed to surface or ground waters by industrial effluents, sewage, septic tank and cesspool percolates, and animal wastes.

When concentration of nitrate in drinking water exceeds 50 mg NO_3^-/L, it becomes a major source of total nitrate intake for humans (WHO, 1993). Although nitrate itself is probably harmless to adults. the hazard to human health occurs from the bacterial conversion of nitrate to nitrite in stomach. When nitrite is absorbed in blood, and converts excess of hemoglobin to methemoglobin, methemoglobinemia may occur. Apart from methemoglobinemia, commonly called Blue Baby Syndrome (BBS), several epidemiological studies have shown

a positive correlation between high nitrate intake and human gastric cancer (Caygill et al., 1986; Weisenburger, 1991). The results of extensive carcinogenesis and metabolic experiments in animals provide strong evidence that formation of N-nitroso compounds which are positively linked with high nitrate intake are likely to be carcinogenic in human (Fine, 1980; "NAS", 1981; Mirvish, 1991). Hence, nitrate needs to be removed prior to use of the water for drinking purposes.

The current maximum allowable concentration for nitrate in drinking water ranges from 2.5 mg N/L in Norway to 23.0 mg N/L in Netherlands, but the United States of America, Canada, Poland, India and many other countries have set 10.0 mg N/L as acceptable upper limit. The European Economic Community (EEC) accepts 11.3 mg N/L or 50.0 mg NO_3^-/L as the mandatory limit for nitrate in drinking water.

Treatment technologies available for nitrate contaminated waters include ion exchange, heterotrophic and autotrophic biodenitrification, chemical denitrification, reverse osmosis, and electrodialysis. Other processes such as membrane bioreactor (MBR) and entrapped mixed microbial cells immobilization (EMMCI) technique are also being examined. For small scale applications, however, ion exchange, using strong base anion (SBA) resins is the most extensively used method. Instability of many SBA resins even in the 20-80° C temperature range with consequent loss of capacity and organic fouling are the main difficulties in using carbon based resins in water treatment applications. In general, tendencies to avoid resin based ion exchangers have been observed

due to susceptibility of release of undesirable organic substances in water and bacterial contamination by resin units This suggests the need for use of inorganic media in water treatment applications.

Sorptive properties of hydrous metal oxides and salts of multivalent metals have been in use since many years. and coated or granulated inorganic media are seriously being evaluated for small scale water treatment. For anions hydrated alumina shows slight preference of Cl^- over NO_3^- (Abe and Ito, 1965) Vesely and Pekarek (1972) noted that Zirconium oxide behaves both as cation as well as anion exchanger. with pH of point of zero charge (pH_{pzc}) at 6.5 and there is slightly higher selectivity towards chloride as compared to nitrate Fritsche (1993) has reported removal of nitrate and other anions by yellow bismuth hydroxide precipitate. Bismuth (Bi) is one of the least toxic of heavy metals and cases of bismuth poisoning in industrial use have not been recorded Therefore. toxicity is not a problem in the handling of bismuth (Howe, 1968).

There is considerable evidence for the association of Bi (III) and nitrate ions in both aquous solutions and solids (Ortel and Plane, 1968). Bismuth nitrate rapidly hydrolyse in water to give basic bismuth nitrate(s) which are insoluble in water. Many bismuth salts, including basic bismuth nitrates, have been used in pharmaceutical and beauticare applications since 17th century. Hence. development and evaluation of bismuth based media for nitrate removal from water for its possible application in drinking water treatment appear promising.

The objective of the present study was to develop and evaluate bismuth based inorganic media for nitrate removal from water. Oxide, oxychloride.

carbonate and hydroxide of bismuth were tested to identify the most promising compound and based on results. use of hydrous bismuth oxide was investigated to assess the merits and limitations of its use in drinking water treatment applications.

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CHAPTER 2

LITERATURE REVIEW

2.1 General Information

2.1.1 Nitrate and Nitrite Intake by Human Beings

Nitrate is present in food and water consumed by human beings. Vegetables, cured meat products and occasionally water are the main sources of the nitrate ingested by human beings, but small amounts are present in cereal products, fruit juice and milk products also. Vegetables that contain considerable amounts of nitrate include spinach, radishes, lettuce, beets and eggplants (Kies, 1981). Nair and Hippalgaonker (1996) reported that average nitrate content in spinach, amaranth and radish foliage grown on sewage irrigation alongwith nitrogenous fertilizers ranges between 230-320 mg N per 100g (dry weight) of vegetable. Nitrate levels in vegetables appear to vary largely from region to region and with the time of year because of the difference in temperature, sunlight, the level of available nitrogen in the soil and soil moisture ("Task", 1978). Nitrate and nitrite have commonly been used to cure meat because they enhance color and inhibit the growth of undesirable microorganism that produce botulism (Fine, 1980). Thus cured meat products can be the major source of nitrate and especially nitrite. Small quantities of nitrite also come from vegetables, fish, cereals and cheese products (Lee et al., 1995). The daily intake

of nitrite by human beings range from 0.10 to 3.40 mg N/person-day ("Nitrate", 1988). In general, vegetables will be the main source of nitrate intake when levels in drinking water are below 10 mg NO_3^-/L. When levels in drinking water exceed 50 mg NO_3^-/L, drinking water will be the major source of total nitrate intake (WHO, 1993).

2.1.2 Health Effects of Ingested Nitrate and Nitrite

Nitrate is probably harmless to humans (Lee et al., 1995). The hazard to human health occurs because of bacterial conversion of nitrate to nitrite. When the nitrite is absorbed in blood and converts excess of hemoglobin to methemoglobin, methemoglobinemia may take place. By reacting with amines and amides in stomach, nitrite may form nitrosoamines and nitrosoamides, some of which have been shown to be carcinogenic in animals. Reports have correlated ingestion of nitrate in drinking water and stomach cancer (Hill et al., 1973), early onset of hypertension (Malberg et al., 1978), increased infant mortality (Super et al., 1981), central nervous system birth defects (Dorsch et al., 1984), non Hodgkin's lymphoma (Weisenburger, 1991), and initiation of kidney diseases (Schultz-Hock et al., 1995). Although, neither the much suspected infant methemoglobinemia, nor the carcinogenic or other effects of nitrate on human health have been proven conclusively, monitoring and regulation of nitrate in drinking water has been felt essential. Additional research is necessary to confirm the relationship, because majority of evidence implicating nitrate as a causative factor is based on correlation studies, which provide only weak

evidence of an association and should not be used to establish a cause and effect relationship (Weisenburger et al , 1991). The standard or guideline values prescribed for nitrate in drinking water are primarily based on retrospective case studies of methemoglobinemia, which have been shown satisfactory from hypothetical toxicological and prospective evidemiological approaches also (Winton et al., 1971). The methemoglobin levels of normal healthy individuals are about 0.5 -2.0% of the total hemoglobin. At levels above 10%, clinical signs are evident. i.e. a bluish color in the skin and lips is produced and the condition is termed methemoglobinemia ("Nitrate", 1988). For toxicolo gical study. the 10% methemoglobin level is chosen, because it is at this level that the disorder first becomes clinically detectable and possibly the infant will remain "barely blue" (Winton et al., 1971). The bluish coloration is attributed to the anoxemia resulting from the decrease in the oxygen transporting capacity in the blood. When the methemoglobin level rises to about 25%, tachypnea weakness, and a rapid pulse rate are observed. Death may occur at levels above 50-60% (Dourson et al., 1991). However, methemoglobinemia responds rapidly to treatment (Lee et al., 1995).

2.1.2.1 Infants Susceptibility for Methemoglobinemia

There are several physiological and biological features of early infancy that explain the susceptibility of infants, less than three months of age, to this disorder. First, the infants' total fluid intake per body weight is approximately three times that of an adult, and so if contaminated water is used for feed

preparation, infants will be affected more than adults Secondly, the incompletely developed capacity of infants for gastric acid secretion allows the gastric pH to become high enough (pH=5-7). This permits the nitrate reducing bacteria to reside in high gastrointestinal tract and reduce the nitrate to nitrite, which otherwise could have been absorbed into the blood circulation and secreted (Cornblath and Hartman. 1948). Nitrite rather than nitrate forms methemoglobin. Thirdly, and interestingly, the predominant form of hemoglobin at birth, Hemoglobin F (fetal hemoglobin), is more susceptible to methemoglobin formation than the adult form of Hemoglobin A, and this fact further predisposes the infant. Finally, there is reportedly decreased activity in the enzyme (NADH-dependent methemoglobin reductase) in infants responsible for normal methemoglobin reduction (Ross and Forges, 1959).

The association between nitrate in water and methemoglobinemia was first described by Comly (1945) who examined two cases of infant methemoglobinemia and also presented data gathered from other doctors who had treated cynosis. All the infants consumed artificial milk prepared with well water high in nitrates. The wells in his study contained 63-138 mg N/L. He considered it inadvisable to use well water containing more than 10 mg N/L in preparing an infant's feeding formula (Lee et al., 1995). Bosch et al, (1950) evaluated 139 cases of infant methemoglobinemia, including 14 deaths, from the records of Minnesota Department of Health. 91% of the cases occurred in infants below two months and 9% between 2 and 5 months. Only for 129 cases, data on water nitrate levels were available. No case was recorded in infants consuming

well water containing nitrate less than 10 mg N/L. Two cases were associated with well water containing 10-20 mg N/L, but available clinical data were insufficient in both the cases and so they were considered questionable All the rest 127 cases occurred with the use of well water containing concentrations greater than 20 mg N/L. Walton (1951) reported the results of a survey performed by the American Public Health Association. A total of 278 cases of infant methemoglobinemia including 39 deaths, were reported, which included the 139 cases evaluated by Bosch et al, (1950). Of the 214 cases, for which data on water nitrate levels were available, none occurred in infants consuming well water having less than 10 mg N/L. Five cases out of 214 were recorded in infants exposed to 11-20 mg N/L. but clinical data on these cases were insufficient for definite diagnosis and therefore, the cases were considered questionable. All the rest 209 cases reported were having nitrate concentrations exceeding 20 mg N/L. These case studies suggest that while water containing less than 10 mg N/L may be taken as safe from infant methemoglobinemia point of view, water source containing nitrate levels between 10-20 mg N/L should also not be rejected outrightly. Based on retrospective epidemiology, hypothetical toxicology and prospective epidemiology methods, Winton et al., (1971) reaffirmed the present recommended nitrate limit (10 mg N/L) in drinking water used for infant intake.

2.1.2.2 Nitrate and Human Cancer

Nitrate intake appears to be a major contributor to gastric nitrite. which is subsequently linked to the formation of N-nitroso compound, potent carcinogens

in experimental animals (Fine, 1980). The results of extensive carcinogenesis and metabolic experiments in animals provide strong evidence that N-nitroso compounds are likely to be carcinogenic in humans ("NAS" 1981). N-nitroso compounds can be classified into two groups: (i) nitrosoamines R_1-N(NO)-R_2, where R_1 and R_2 are aryl groups; and nitrosoamides R_1-N(NO)CO- R_2, where R_1 is an alkyl group and R_2 is an aryl group ("Task", 1978). Several epidemiologic studies have shown a relationship between high nitrate intake and human gastric cancer (Caygill et al., 1986. Weisenburger, 1991) However, there is presently no conclusive evidence that nitrates are the causes for human gastric cancer. To compensate for the lack of data related directly to cancer incidence in human, data obtained from animal experiments are often used to estimate the human cancer risk. Such interspecies conversion from animals to humans is performed under the assumption that nitrate salts have similar carcinogenic effects in humans as in animals. However it is very difficult to extrapolate from the results of animal experiments the dosages that will increase cancer incidence in the human population (i.e. 1 in 1 00 000 or less). Also the difficulty in extrapolating animal results involves lack of concordance of cancer site (target organ), cancer mechanism and frequency of response. Because of these difficulties, the interspecies conversion process is associated with uncertainty (Lee et al., 1995).

2.1.3 Nitrate Standards for Drinking Water

Although many correlation studies of high nitrate and other diseases have been reported, non-carcinogenic acute toxicity of nitrate due to methemoglobin is

the basis of most nitrate standards in drinking water The current maximum allowable concentration for nitrate in drinking water supplies ranges from 2.5 mg N/L in Norway to 23.0 mg N/L in the Netherlands (Rittman and Huck. 1989). Table 2.1 gives the nitrate standards for potable water prescribed by different countries/organisations.

Table 2.1

Nitrate Standards for Drinking Water

S.No.	Country/ Organisation	(mg N/L)	(mg NO$_3$/L)	Remarks / References
1.	Norway	2.50	11.0	Rittman and Huck (1989)
2.	EEC	5.65	25.0	GV; Cotruvo & Vogt (1990)
3.	Bulgaria	6.70	30.0	Lunkad (1993)
4.	USEPA	10.00	45.0	MCL; Cotruvo & Vogt (1990)
5.	Canada	10.00	45.0	MAC; Cotruvo & Vogt (1990)
6.	Poland	10.00	45.0	Lunkad (1993)
7.	India	10.00	45.0	CPHEEO (1984)
8.	WHO	11.30	50.0	GV; WHO (1993)
9.	EEC	11.30	50.0	ML ; Cotruvo & Vogt (1990)
10.	Netherlands	23.00	102.0	Rittman and Huck (1989)

GV : Guideline Value; MCL: Maximum Contaminant Level;

MAC : Maximum Allowable Concentration; ML : Mandatory Limit.

EEC: European Economic Community.

USEPA: United States Environmental Protection Agency

WHO: World Health Organisation

Similar to United States (US), Canada and Poland, Indian Standards

recommend 45.0 mg NO_3^-/L (equivalent to 10.0 mg N/L) as "acceptable" as well as "cause of rejection" of source for nitrate in drinking water As a result of recent evidence of the presence of nitrite in some water supplies, WHO (1993) concluded that a guideline value for nitrite should also be proposed. Accepting a relative potency for nitrite and nitrate with respect to methemoglobin formation as 10:1 on molar basis, a provisional guideline value of 3 mg NO_2^-/L has been proposed for drinking waters (WHO, 1993). Health and Welfare Canada has recommended 3.2 mg NO_2^-/L as maximum acceptable concentration (MAC) for nitrite ("Guidelines", 1993). Because of the possibility of simultaneous occurance of nitrite and nitrate in drinking water supplies, the sum of the ratios of the concentration of each to its guideline value should not exceed 1 i.e.

$$\frac{Cnitrate}{GVnitrate} + \frac{Cnitrite}{GVnitrite} \leq 1$$

Where C = Concentration

GV = Guideline Value

2.1.4 Sources of Nitrate in Water Bodies

Background nitrate concentrations in surface waters are usually below 5 mg N/L, and higher concentrations are often observed in ground water (Fraser et al., 1980). In farmed areas, ground water nitrate contamination originates mainly from the excessive application of animal manures (Pratt and Jury. 1984), and commercial nitrogenous fertilizers (Dahab and Lee. 1988). Nitrate may also be contributed by industrial effluents; animals wastes: domestic sewage. septic tank and cesspool percolates. Industries discharging waste waters containing high

concentrations of nitrate or nitrite include fertilizer manufacturing, iron and steel production, munition manufacturing, cattle feed lots, swine and poultry processing, electronic component manufacturing, nuclear fuel processing and uranium oxide fuel fabrication (Patterson, 1985). Industrial wastes may not contain nitrite or nitrate initially, but they may be potential sources of these nitrogen compounds if they contain ammonia and are treated biologically (Patterson, 1985).

The main direct sources of nitrate nitrogen in ground water are commercial fertilizers, animal manures and fixation by the rhizobium-legume symbiosis in agriculture (Pratt and Jury, 1984); landfill leachates and unscientific onsite sewage disposal practices including septic tanks and cesspoools (Hantzsche and Finnemore, 1992). Nitrates are also contributed by industrial wastes and domestic waste waters (Lee et al., 1995).

Nitrate levels over vast agricultural terrain can be correlated with the use of nitrogenous fertilizers and ground water development (Lunkad. 1993). The build up of nitrates in ground water in populated area is largely a cummulative effect of septic tank effluents, landfill leachates and cesspool percolates. Localised high nitrate level may be suspected from some industrial sources.

Ground water nitrate contamination originating mainly from agricultural sources have been reported by; Spalding and Exner (1991) for United States; Gillham (1991) for Southern Ontario, Canada; and Chilton and Foster (1991) for central and eastern England. In India, maximum nitrate concentration reported in some ground water samples from Haryana, Punjab and Uttar Pradesh in north.

Tamil Nadu and Karnataka in south, Orissa and Bihar in east and Gujrat in west also parallels high nitrogenous fertilizer consumption (Lunkad, 1993) Excess nutrients in irrigation return flow, if not properly drained off, gradually infiltrates into aquifer. Contamination of ground water around populated areas of Lucknow and Jodhpur (India) are examples of contamination from urban sewage. septic tank and cesspool percolates alongwith industrial source leakages.

2.1.5 Nitrate Levels in Terrestrial Waters and Contaminated Ground Waters

Terrestrial waters include polar ice-caps, water frozen at high altitudes, water stored in prestine lakes,.and rivers and subsurface rock formations. Nitrate level in relatively pollution free areas of continents such as high altitude lakes and rivers and snow clad mountains help in understanding the anthropogenic nature of this pollutant in ground waters. In central Himalayan snow and ice, the nitrate level is about 0.5 mg NO_3^-/L (Lunkad, 1993). The average nitrate in world rivers is about 1.0 mg NO_3^-/L which is close to its content in Himalayan rivers .viz., Bhagirathi (0.31-0.99 mg NO_3^-/L), Alaknanda (Ganga source waters) (0.99 mg NO_3^-/L), and Ganga at Rishikesh (0.81 mg NO_3^-/L). The slight increase of nitrate in river waters compared to that of frozen-water may be due to contributions from biochemically derived soil-nitrate. It thus emerges that in a relatively pure system, surface water contains less than 1.0 mg NO_3^-/L and its higher concentrations in ground water, therefore reflects anthropogenic contributions (Lunkad, 1993). In oceans, which are the ultimate sink for terrestrial waters, average nitrate level is 0.67 mg NO_3^-/L (Mason and Moore, 1985). This is

slightly lower than the value in average river water indicating possible biochemical removal by marine planktons (Lunkad. 1993).

Nitrate levels in water sources, particularly ground water is rising in most countries of the developed world. Ground water nitrate contamination is widespread in the United States (US) and especially prevalent in agriculture intensive areas such as Texas. Oklahama, Kansas, Nebraska. Iowa, South Dakota. and eastern Colorado (Spalding and Exner, 1991). Nitrate as a major contaminant in ground water were reported by 75% of the states in US where 23% of violation of primary drinking water standard were the results of excessive nitrates (Bouwer and Crowe, 1988). The highest incidence of contamination occurs in ground water in the middle of the contiguous USA where nitrate levels in about 20% or more of the sampled wells in Iowa, Nebraska and Kansas exceeded the Maximum Contaminant Level (MCL). In contrast, the incidence of contamination is lower in Texas (8.2%) and very low in North Carolina (3.2%) and Ohio (2.70%) (Spalding and Exner, 1993). Nitrate in ground water of several agricultural areas in Southern Ontario, Canada also exceeds 10 mg N/L (Gillham, 1991). Fried (1991) reported that by 1995, more than 10 million French, about 20% of the population, will drink water exceeding the European Community (EC) limit of 11.30 mg N/L. Eight percent of the public water works in Denmark and 5% of those in former Federal Republic of Germany supply ground water that exceeds the EC limit for nitrate and in both the countries unprotected aquifers are contaminated with nitrate. Increased degradation of drinking water and eutrophication of coastal waters in the European Community are consequences

of steadily increasing nitrate levels in surface, ground and coastal waters. In areas of Belgium where agriculture has adversely affected ground water quality, nitrate concentrations range from 4.0 to 11.0 mg N/L. Increasing levels of nitrate in the ground water of the Netherlands eventually will effect 25% of the well fields (Fried. 1991). In eastern and central England. nitrate concentrations are increasing in the ground water which provides 30 to 50% of the drinking water The number of ground water sources containing nitrate concentration over 50 mg/L increased from 60 in 1970 to 105 in 1984 and 142 in 1987 and from 154 in 1989 to 192 in 1990 (Chilton and Foster, 1991). Nitrate contamination of ground water is also a growing problem in Caribbean, Africa, the Middle East. Australia and New Zealand. Ground water quality in two major catchments of Barbados is already affected by agricultural inputs. Concentrations in the urban areas were consistently above 10 mg N/L and reflects nitrogen loading from high density housing with unsewered sanitation (Chilton. 1991). Faillat (1990) reported nitrate contamination of ground water beneath areas of the Ivory Coast that were deforested and used for either crop production or settlements.

In Israel, about half of the water wells in the, coastal aquifer, supplying about 30% of the total water consumption exceeds the prescribed standard for nitrate (Green and Shelef, 1994). Sewage effluent is an important source of water for agriculture in Israel and other semi-arid areas with limited ground and surface water. In Israel. nitrate contamination of shallow ground water beneath sewage irrigated land was attributed to applications of fertilizer and sewage effluent (Ronen and Magaritz, 1985). Nitrate-nitrogen levels in one third of the

bores sampled on the Gambier Plain in south east South Australia exceeded 10 mg/L (Dillon et al., 1991). Leachates from leguminous pastures grazed by livestock were the source of most of the nitrate in the ground water, whereas nitrate in wastes from dairies, sale yards, and milk and meat processing facilities were responsible for the highest concentrations (Dillon et al., 1991). In New Zealand unconfined aquifers often are extensively contaminated by nitrate, which is associated with intensive grazing on non-irrigated grass-clover pasture, grazing on irrigated pasture and fertilization of crop and horticultural land (Burden, 1982).

In India, a rapid reconnaissance of nitrate in shallow ground waters was done by Central Ground Water Board (CGWB) (Handa, 1986). This study reported average concentration of nitrate in well waters (mostly from dug wells) from several states, namely Andhra Pradesh, Bihar, Delhi, Gujrat, Haryana, Himachal Pradesh, Jammu and Kashmir, Madhya Pradesh, North Eastern States, Orissa, Punjab, Tamil Nadu, Uttar Pradesh and West Bengal with exclusion of Goa, Karnataka, Kerala, Maharashtra and Rajasthan. Although the author mentioned towns and districts where concentrations exceeded 22.6 mg N/L, the number of samples analysed statewise was not indicated, and no discussion was given as to possible sources of pollution in different regions. In Haryana, the highest nitrate concentration in ground water was reported from Hissar (406.32 mg N/L) and Mahendragarh (365.68 mg N/L). In another study (Kumar and Singh, 1990), out of 49 samples from Mahendragarh district (Haryana), only 13 samples (27%) showed nitrate concentration less than 10 mg

N/L, 10 samples (20%) between 10.0 – 22.6 mg N /L and 26 samples (53%) was above 22.6 mg N/L. Bulusu and Pande (1990) reported the study undertaken by National Environmental Engineering Research Institute (NEERI). Nagpur. covering selected districts from 17 Indian States (including Rajasthan and Karnataka. which were not reported earlier. but excluding North Eastern States. Goa and Kerala. In 27% out of a total of 4696 samples analysed. the nitrate concentrations were found above prescribed limit of 10 mg N/L. In area specific study, Nawlakhe et al., (1995) reported 46.5% of 114 samples from Shivpuri district (Madhya Pradesh) to be having more than permissible nitrate. Somasundram et al., (1993) reported that out of 93 ground water samples taken from Madras Urban aquifer, 70% showed the nitrate levels exceeding 10 mg N/L. and maximum concentration reported was 225 mg N/L. Tamata et al., (1992) reported that around 18% samples from Bangalore city of Karnataka contained more than 11.28 mg N/L nitrate and maximum level was 45.15 mg N/L. Swami (1991) reported ground water cotamination due to nitrate in Cuddapah district of Andhra Pradesh. Sukhija et al., (1989) reported concentrations upto 79.00 mg N/L below Tirupati town in Andhra Pradesh. Sahagal et al., (1989) reported that in alluvial aquifer below Lucknow out of 52 wells monitored in 1981, nitrate concentration in 21 wells (40.4%) was more than the permissible limit. In 1988. out of 46 sampling stations. 52.2% had nitrate more than the prescribed limit. indicating increasing extent of nitrate contamination. The highest observed concentration was 650 mg N/L.

Nitrate contamination of ground water, is however, relatively lower and

perhaps minimum in the northern and north eastern extra-peninsular India. In a study of 34 ground water samples from Guwahati (Assam), nitrate concentrations above 10 mg N/L was detected in only 2 samples, (i.e. 6%). In 8 samples (23.5%) the concentration ranged from 0.02 to 0.23 mg N/L and in another 15 samples (44%)) the range was 0.23 to 2.5 mg N/L (Prakash et al., 1992).

2.2 NITRATE REMOVAL METHODS IN WATER TREATMENT

Prevention of its entry into the ground water appears to be the best approach for nitrate pollution control. However, the anticipated results will be achieved only after one to four decades due to long transportation time through the unsaturated zones, which also depends on the depth of water table (Green and Shelef, 1994). Therefore, application of advanced treatment technologies is inevitable and justified alternative in order to meet the required nitrate levels in near future.

Nitrate removal methods in water treatment are basically of two types: (i) Elimination Processes, and (ii) Separation Processes. Whereas, chemical and biological (biochemical) methods remove nitrate from water by reductive elimination process, reverse osmosis, electrodialysis and ion exchange are physicochemical methods using separation technique for nitrate removal from water.

2.2.1 Chemical Methods

Nitrate removal from water can be achieved using chemical methods of denitrification. Both catalysed and uncatalysed processes have been studied

extensively Various catalysts, e.g . Cu, Al, Pd etc. have been examined. Buresh and Moraghan (1976) studied the copper catalysed reduction of nitrate by ferrous iron The reduction can be induced under basic pH conditions according to following reaction:

$$NO_3^- + 8Fe (OH)_2 + 6H_2O = NH_3 + 8Fe (OH)_3 + OH^- \tag{2.1}$$
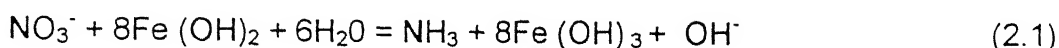
Experimental results showed that a Fe: NO_3^- ratio of about 15:1 was required in presence of a copper catalyst for the reaction to proceed. This process generated large quantities of iron sludge. and formed ammonia that requires removal by air stripping. Sorg (1978) discouraged its applicability due to high cost associated with the process. Peterson (1979) investigated uncatalysed reduction of nitrate by Fe (II) at an elevated temperature of 75°C. The maximum-rate of reaction was around pH = 8.0. The rate of reaction became very slow when pH fell down to 6.0 due to reduction of nitrate. Hecke et al., (1990) studied the presence of ferrous iron and copper together considering that both of them form a redox couple. In the batch system, the reaction was slow at pH 7.5, but became very fast at pH 8.1. For a reasonable rate of reaction, the optimum pH suggested was 7.7. In a continuous system, a reduction of more than 50% of nitrate was reported possible. Of the different reduction products, only NH_4^+ - N posed some problems and its minimization was considered important.

Murphy (1991) has reported chemical denitrification using aluminium powder. The reduction was explained assuming following reaction:

$$3NO_3^- + 2Al + 3H_2O = 3NO_2^- + 2Al + OH)_3 \tag{2.2}$$

$$NO_2^- + 2Al + 5H_2O = NH_3 + 2Al(OH)_3 + OH^- \tag{2.3}$$

$$2NO_2^- + 2Al + 4H_2O = N_2 + 2Al(OH)_3 + 2OH^- \tag{2.4}$$
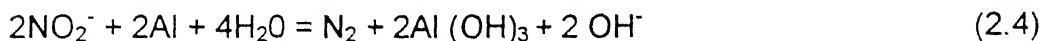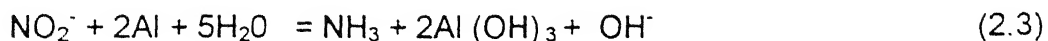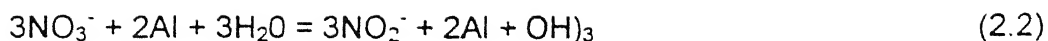
In a pH range of 9 00 - 10 50, selective reduction of nitrate relative to sulfate was reported to be possible, and between pH 9.1 and 9.3, loss of reductant through decomposition of water could be minimized to less than 2%. The authors felt that the subsequent control of pH, concentration of dissolved aluminium, nitrite and ammonia at a realistic cost may make this process potentially useful for combating nitrate pollution (Murphy, 1991). Based on the assumption of a total (and only) ammonia formation during reduction of nitrate, it was estimated that 1.16g of aluminium should be required to reduce 1.0g of nitrate (Murphy, 1991).

In another study, Boleslav and Pitter (1992) reported that the reduction of nitrate by ferrous iron in presence of copper sulfate catalyst is affected by the ratios of ferrous to nitrogen, and alkalinity. The observations were made between pH 7.2 - 12.4, Fe/N ratio between 5-11:1 and OH^-/Fe ratio between 1.2 - 3.6 : 1. In a weakly alkaline media, the reduction rate was low, but formation of nitrite was minimum and less than 40% of the nitrate could be converted to nitrogen gas. In a strongly alkaline media, the reduction rate was high, but the main reaction product was nitrite.

Horold et al., (1993) reported that use of palladium on alumina in presence of hydrogen gas was suitable for reduction of nitrate mainly to nitrogen. Only small amount of ammonia was formed as by product (98% nitrogen and 2% ammonia). Use of bimetallic catalyst was also suggested and copper - palladium catalyst was found to give excellent results (e.g. nitrate removal activity of 3.13 mg NO_3^- per minute per g catalyst). Compared to biodenitrification, the catalyst were reported to have 30 times higher nitrate removal activity.

Shell (1993) also described catalytic nitrate reduction using gaseous hydrogen with palladium - copper supported on alumina, under "SOLVAY KNR" process. Tacke et al., (1993) reported the kinetic aspects of nitrate reduction by hydrogen with alumina supported palladium and copper doped palladium. The reaction conditions (H_2 pressure, temperature and pH) were optimized with respect to the intermediate formation of nitrite and ammonium ion. A daily nitrate removal of 51.0 mg/m^3 was attainable in a alumina supported palladium (5%) enclosed in a continuously operated lab. system (Tacke et al., 1993).

Following a rather different approach, using photochemical method rather than catalytic chemical reduction of nitrate, Princz et al., (1988) studied the photoreduction of nitrate in the presence of organic compounds. The process is reported to be multistep reaction which generally results in intermediate and derivatives like NO_2^-, NH_4^+, $H_2N_2O_2$ etc. When the irridiation was carried out at pH 8.0 in the presence of 20 - 50% surplus of organic material, the formation of derivatives could be avoided. The main advantage of the method is that no special chemicals or microorganisms are needed. Methyl or ethyl alcohol or other

products of the food industry can be applied as organic compound and sodium bicarbonate can be used for pH adjustment. With ultravoilet light. apart from denitrification' sterlization of water is also accompanied. Due to its simplicity. the process is recommended for domestic use The capacity of the process is 3-4 L nitrogen free water per kwh in the range of 100-200 mg/L of nitrate concentration.

2.2.2 Biological Methods

Biological denitrification is a well established process in wastewater treatment, but the transfer of this process to water treatment side has been rather slow because of the possible bacterial contamination of treated water supply. Since mid 1980s, however, a number of experimental demonstration plant as well as full scale treatment plant have been established and operated

Biological denitrification is the dissimilatery reduction of nitrate or nitrite to nitrogen gas through gaseous nitrogen oxides. Generally denitrification is considered to be an anoxic process carried out mostly by facultative bacteria. i.e. bacteria capable of utilising nitrate as well as oxygen as electron acceptors. The reduction of nitrate to nitrogen gas proceeds through four steps :

$$NO_3 \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (2.5)$$

$$(1) \quad (2) \quad (3) \quad (4)$$
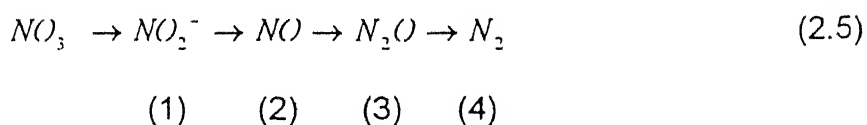
Ability of bacteria for denitrification is diverse with many bacteria performing only part of these consecutive steps. Any one of the last three steps can be the final one, depending on the species of bacteria involved and pH of water. The process of denitrification, because of its similarity to oxygen

respiration, is called "nitrate respiration". The energy yield of "nitrate respiration" is slightly lower than that of oxygen respiration, (Green and Shelef, 1994), e.g.

$$5C_6H_{12}O_6 + 24KNO_3 \rightarrow 30CO_2 + 18H_2O + 24KOH + 12N_2, \Delta H = -570\,kcal$$

per mol glucose   (2.6)

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad ; \Delta H = -686 \text{ kcal/mol. glucose} \qquad (2.7)$$
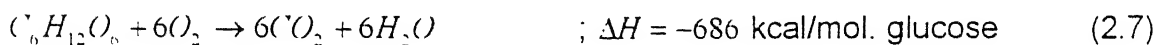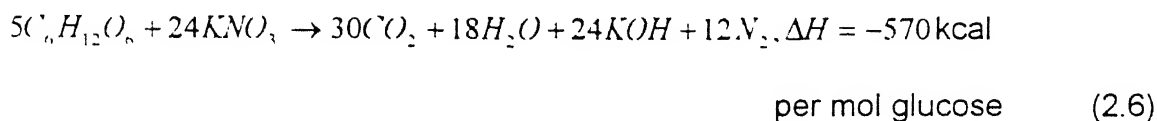
Due to lower energy yield, denitrification is inhibited by oxygen in the majority of denitrifying bacteria. Oxygen concentration ranging from 0.1 to 0.2 mg/L have been indicated to have inhibitory effects on denitrification (Rittman and Huck, 1989). Most of the denitrifiers are heterotrophic bacteria, and can use a variety of organic carbon sources, with methanol, ethanol and acetic acid being the most widely used in water treatment. Gaseous organic substrates such as methane and carbon monoxide can also serve as substrate for denitrification in water. Commonly found heterotrophic denitrifying species belong to the Pseudomonas, Alcaligones and Flavobacterium bacterial genera. Denitrification can also be carried out by autotrophic bacteria, which do not require an organic carbon source for energy derivation. Hydrogen and reduced sulfur compounds serve as the substrate and carbon dioxide or bicarbonate serve as the carbon source for cell synthesis. Thus, biological process of denitrification is of two types: Heterotrophic Denitrification and Autotrophic Denitrification.

2.2.2.1 Heterotrophic Denitrification

This is the most studied and widely used biological commercial process for ground water nitrate removal. In this process, an organic carbon source is

used as the electron donor. Methods for denitrification are primarily characterized by the way in which the bacteria are retained in the system, and the carbon and energy source. Ethanol is the most common carbon source used followed by methanol and acetic acid (Green & Shelef, 1994). Besides an organic carbon source, phosphate addition is also required.

High biomass concentration in the denitrification reactor is usually obtained by the biological sludge attachment to solid media, which is either stationary (fixed bed), moving (rotating discs), or fluidized (fluidized bed). These types of reactors are well suited to conditions of low substrate concentrations and high flow rates, which are typical in ground water denitrification processes. Posttreatment is always required since the effluents from the denitrification reactor contain microorganisms, carbon source residuals, organic matters resulting from bacterial activity, nitrites and no dissolved oxygen. Conventional posttreatments include aeration (for nitrite and dissolved oxygen increase), filtration (for carbon source residuals and organic matters) and disinfection (bacterial mass).

Gaunlett and Craft (1979) conducted a pilot-scale study for the removal of nitrate from the Thames water. Three type of upflow denitrifying reactors were tested using methanol as an organic carbon source : (1) a packed column with two grades of gravel as a bacterial support medium; (2) a suspended growth reactor with a floc blanket of denitrifying bacteria growing on fine river silt; and (3) a fluidized sand bed reactor. The reactors required start up period of two weeks to establish sufficient bacterial populations. The highest denitrification rate per

unit reactor volume was observed for the fluidized sand bed (160 g N/m^3 h at 10^{0}C) and the lowest for the packed bed reactors (12 g N/m^3 h at 10^{0}C). A suitable upflow velocity for a low temperature operation (0-10^0 C) was observed to be 12 m/h for suspended growth and 15-20 m/h for fluidized sand bed reactors. Nitrate concentrations were reduced by approximately 45 mg/L even at 2^0 C in the fluidized sand bed reactor Based on these results, the first European full scale denitrification plant was constructed at Bucklesham, Great Britain. in 1982. Hall and Zabel (1984) reported its performance during 2 years of its operation. The plant had the design capacity of 115 m^3/h with an upflow filtration rate of 22 m/h. The plant operated successfully for two years and removed 14 mg N/L at as low a temperature as 2^0 C, using a methanol dose of 45 mg/L. To achieve optimal biological growth. dosing with phosphoric acid was necessary to increase the phosphate concentration from background of < 1.0 mg P/L to between 0.2 to 0.4 mg P/L depending on the methanol dose applied. This yielded a C : P ratio of 56:1. To avoid excess carbon entering the distribution system, the plant was operated carbon-limited with a residual 3.5 mg N/L in treated water. Operating the plant carbon limited resulted in occasional nitrite concentrations of upto 2 mg N/L requiring sufficient chlorination capacity for removal. Although the above plant was designed for removal of nitrate from river water, fluidized sand bed technology is equally applicable to the treatment of ground water. The disadvantage of this approach is that the required secondary treatment is not always available at ground water sources, particularly in remote areas. Soares et al., (1988) conducted denitrification studies on ground water (22.6 mg N/L) using

a downflow sand column with an initial porosity of 32%. Denitrification was achieved using sucrose as substrate and most of the microbial activity was located in the top 15 cm of the sand column. Complete removal of nitrate was achieved at a C : N ratio of 2. Column operation was affected by the nitrogen trapped in the column, and application of vacuum successfully restored the reactor

Dahab and Lee (1988) evaluated the denitrification performance of static bed upflow reactors using spherical support media (25 mm diameter) or cylindrical rings (16 mm diameter). The reactors operated effectively at an influent concentration of 100 mg NO_3/L for 10 months using acetic acid as the carbon source. Complete nitrate removal was observed at a C:N ratio of 1.5 and a minimum retention time of 9h. Effluents were high in suspended solids and turbidity.

Kappelhof et al., (1992) reported the results of effectiveness of three kinds of support media in upflow fixed bed denitrification reactor using ethanol as substrate. Amongst expanded schist, anthracite and sand; sand was found to be the preferable media because the bio mass could be removed with simple rinsing procedures.

Liessens et al., (1993b) studied the performance of a biological fluidized sand bed denitrification plant of 0.25 mgd capacity at de Blankaart. Belgium. Methanol was used as a substrate. Complete nitrate removal was observed for an influent concentration of 75 mg NO_3/L and an empty bed contact time of 15 minutes. The reactor loading was 9.0 kg $NO_3^- / m^3 - d$ at 3.5^0C. Nitrite was not

detected in presence of 1-2 mg/L of excess methanol. Methanol requirements were observed to be 20-25% more than the amount calculated based on stoichiometry. Biomass was removed from the sand particles using a stirrer and a hydrocyclone Posttreatment included a trickling filter and granular activated carbon (GAC) columns for the removal of methanol from treated water. Liessens et al, (1993a) studied the effects of microbial treatment on water quality Residual methanol and microbial excretion product increased the dissolved assimilable organic carbon (AOC) in the reactor effluent. *Hyphomicrobium sp.* was observed to be an important methylotrophic denitrifier. Hydraulic shear caused the washout of a diverse number of bacterial strain, resulting in log increases of 2.4, 0.7, 1.8, 0.61, 1.5. and 1.0 in the number of total coliforms, fecal coliforms, fecal streptococci, Aeromonads, Clostridia, and Staphylococci, respectively in the treated water. The effluent required post treatment, which included filtration and disinfection to ensure removal of residual organic carbon and prevent the break through of indicator organisms. McCleaf and Schroeder (1995) developed a membrane immobilized biofilm reactor in which denitrifying bacteria and carbon energy source were segregated from the water to be treated. Nitrate ions from water diffuse through the membrane (0.2 µm), to the other side of the membrane. The substrates and the nutrients were supplied from the biofilm side of the membrane. The diffusion of methanol from the biofilm side to the water being treated was observed. Reising and Schroeder (1996) further studied the nitrate removal using both biofilms and suspended culture by decreasing the membrane pore size to 0.02 µm to minimize the microbial

contamination of the product water side of the membrane. Suspended culture provided higher nitrate removal than biofilms

The use of cellulose in the restoration of nitrate contaminated ground water by biological methods has been described by Boussaid et al. (1988). In their study, denitrification reactors were packed with a mixture of straw and maerl, or with sand and maerl. Posttreatment was carried out by reinfiltration of the effluent back into the aquifer. Volokita et al. (1996) described the use of newspaper as carbon source for biological denitrification in laboratory packed bed reactors. Newspaper straded pieces served as the sole carbon and energy substrate as well as the only physical support for the microbial population. Complete removal of 100 mg NO_3^-/L was readily achieved without accumulation of nitrite. The treated water contained low dissolved organic carbon (4-10 mg/L). The cellulose dependent denitrification process was sensitive to changes in temperature. The nitrate removal rates at 4^0C were approximately one third of the rates observed at $32^0 C$. The newspaper matrix of bed allowed the free release of evolved gas and no clogging was observed. Three commercial heterotrophic water denitrification processes viz. NITRAZUR, BIODENIT and DENIPOR are at present being widely used. Five treatment plants for the biological removal of nitrates from water have been installed in France since 1983 and several other plants are being installed in Germany and Italy (Green and Shelef, 1994).

The "NITRAZUR" process, developed by DEGREMONT is a heterotrophic process presently using ethanol (previously acetic acid) as the carbon source. The first commercial treatment plant using NITRAZUR process was installed in

Chateau-London, France. in 1983. The denitrification reactor operates in an upflow mode and BIOLITE particles 2.7 mm in diameter are used as the biomass carrier. Posttreatment includes aeration, filtration through granular activated carbon and disinfection by chlorination. The reactor is washed by air and water simultaneously in order to avoid accumulation of aging biomass which might cause nitrite accumulation at the reactor outlet. Ethanol requirement is 0.90 g/g of nitrate removed and that of phosphate is about 0.025 g/g of nitrate removed. The system produces 18.0g of sludge per 100g of nitrate removed (Richard, 1989). A "NITRAZUR" plant operated at Champfleur, France, yielded a nitrate removal efficiency of 72% for a continuous flow of 35 m^3/h and an ethanol dose of 3.10g/g of nitrate-nitrogen removed.

The principle of the "BIODENIT" process, developed by OTV, is based on conventional sand filtration, i.e. water flows downwards under slight pressure on a mineral medium having a grain size between 2 to 5 mm. In France, the first commercial drinking water facility was constructed in Eragny, in 1983 for 80 m^3/h and a similar installation with 400 m^3/h was built at Dennemont. in 1987 consisting of four fixed bed denitrification reactors and four postfiltration units. Ethanol and phosphorous are added in the reactor. The nitrate removal efficiency is about 74% with an ethanol dose of 1.20 g/g of N removed. The sludge production is 32 kg/d and is discharged to sewer (Rogalla et al., 1990). The treated water is polished through an aerated two-layer sand-activated carbon filter called "Biocarbone" before ozonation and chlorination. The final quality after posttreatment is comparable to raw ground water except for the low nitrate

levels. Operational problems of clogging of polishing filter and nitrite formation were prevented by intensifying the backwashing cycle. A typical cycle lasts for 48h. with a one-hour washing period (Rogalla et al., 1990).

Roennefahrt (1986) developed the DENIPOR process in Germany for removal of nitrate from ground water. The process utilizes heterotrophic microorganisms present in aquifer A buoyant, spherical synthetic material, styropor, made of expanded polystyrene was used as biomass support for fixed bed reactors. The use of such synthetic biomass support material overcome problems of clogging and excess biomass was easily removed from the support material during downward flushing. Ethanol was used as the substrate and phosphate was added as nutrient. Posttreatment is accomplished by aerobic biological filtration through anthecite and sand, followed by chlorination. The first large-scale treatment plant of this kind was installed in Langenfeld and Monheim in Germany. A nitrate removal efficiency of 90% was achieved, with nitrate loading rate of upto 1.50 kg/m^3d. The recirculation rate was 200-500%. Ethanol requirement is 0.60-0.70 g/g of nitrate removed. About 0.09-0.135 g sludge is produced per g of nitrogen removed. Higher loading rates of upto 5.40 kg/m^3d reduced the reliability of the system due to excessive growth of biomass, which could not be flushed out from the carrier fast enough. Formation of nitrite was prevented with the addition of sufficient ethanol.

2.2.2.2. Autotrophic Denitrification

Autotrophic denitrification refers to the dissimilatory reduction of nitrate to nitrogen by autotrophic bacteria. These bacteria use sulfur, sulfur derivatives or

hydrogen as electron donor to derive energy from their oxidation and carbon dioxide or bicarbonate as carbon source for cell growth. No organic carbon source is required for autotrophic denitrification. Sulfur and its derivatives are used by Thiobacillus denitrificans. while Paracoccus uses hydrogen (Green and Shelef. 1994).

Autotrophic denitrification using sulfur or sulfur derivatives has been studied by several investigators in laboratory and pilot-scale experiments. The following stoichiometric relationship have been reported (Green and Shelef, 1994) ·

(1) Sulfur

$$55S + 50NO_3^- + 38H_2O + 20CO_2 + 4NH_4^+ \rightarrow 4C_5H_7O_2N + 25N_2 + 64H^+$$
$$+ 55\ SO_4^{2-} \quad (2.8)$$

(2) Sulfides

$$5S^{2-} + 8NO_3^- + 8H^+ \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O \qquad (2.9)$$

(3) Thiosulfate

$$5S_2O_3^{2-} + 8NO_3^- + H_2O \rightarrow 4N_2 + 10SO_4^{2-} + 2H^+ \qquad (2.10)$$

(4) Hydrogen

$$5H_2 + 2NO_3^- \rightarrow N_2 + 4H_2O + 2OH^- \qquad (2.11)$$
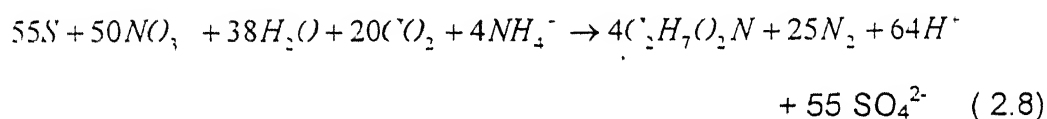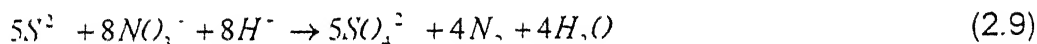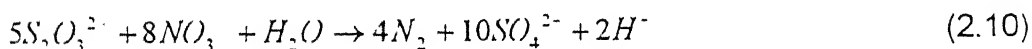
Driscoll and Bisogni (1978) reported the use of sulfur and sulfide in packed bed reactors for autotrophic denitrification, using Thiobacillus denitrificans. The biochemical reactions seemed to be hydrogen ion producing and so limestone was used to supplement the alkalinity consumption. The nitrate-nitrogen was reduced from 24.0 to 1.1mg N/L under nitrate limiting growth

conditions. The minimum hydraulic retention time required for complete nitrate removal decreased from 14h to 4h with decreasing geometric mean sulfur particle size from 1.55 to 0.39cm. Although limestone compensated the alkalinity consumption during denitrification, it added hardness and total dissolved solids (TDS) to the effluent. Schipper et al., (1987) reported their observations of pilot plant study using sulfur and limestone for denitrification. A filtration rate of 0.50 m^3 / m^2.h in upflow mode was used, similar to the rate used in slow sand filtration. 20 mg/L of phosphate was added to the influent. While the sulfate concentration increased five folds, the bicarbonate alkalinity almost doubled during the process. Lewandowski et al., (1987) encapsulated autotrophic denitrifiers in calcium alginate beads containing sulfur and calcium carbonate to evaluate autotrophic denitrification in a completely mixed batch reactor. Nitrate concentrations were reduced from 27 to 6 mg/L in 7h. The denitrification rate reduced from 4.6 to 2.4 mg N/L after approximately 2h. Kruithof et al., (1988) observed a nitrate-nitrogen reduction from 20 to 3.5 mg N/L at a filtration rate of 0.25 m^3/m^2.h in a filter consisting of gravel layer (2-6mm) overlying a mixture of sulfur (2-6mm) and limestone (2-5mm). Nitrate removal of 0.18 kg N/m^3d, and biomass yield of 0.23 per g of nitrate removed were observed. The cascade tray was used to aerate the treated water and infiltration was achieved using the pond. As reported by Hijnen et al., (1988), the AOC concentration of the treated water ranged from 100 to 500 µg acetate. C eq./L. and was due to algal growth. As sulfur-limestone filtration process increases sulfate concentration and hardness of finished water. Kool (1989) suggested that this method is well suited

for water with low hardness and sulfate levels Hoek et al., (1992) reported the optimization of sulfur - limestone filtration process of autotrophic denitrification. Due to anaerobic conditions in the filter, sulfide production used to take place, which affected the infiltration of the denitrified water in the infiltration pond. Oxidation of sulfide in the cascade and infiltration pond to colloidal sulfur form resulted in clogging of bottom of the infiltration pond. Hence, to avoid this, they recommended a sulfur to limestone volumetric ratio of 1:2 to be used in the filter bed.

Hydrogen, being inherently clean and only very slightly soluble in water (1.6 mg/L at 20°C) may be a good reactant and hence many investigators have studied autotrophic denitrification using hydrogen. The reaction can be written as :

$$2NO_3^- + 5H_2 = N_2 + 4 H_2O + 2OH^- \qquad (2.12)$$

Stoichiometrically, 0.35 mg   of hydrogen are required for complete denitrification of 1.0 mg N .

Kurt et al., (1987) studied hydrogenotrophic denitrification using a fluidized bed sand reactor. The optimum pH for nitrate removal was 7.5. Nitrite accumulated when the pH was above 9.0. A residence time of 4.5h was required for complete denitrification of water that contained 25 mg N/L.

Dries et al., (1988) reported the hydrogenotrophic denitrification using polyurethane as support media. The nitrate-rich water was entered from the top of a downflow column and hydrogen gas entered from the bottom of the column.

The water then entered a second reactor in upflow mode where the residual hydrogen was consumed. In the upper part of the column, water was aerated and nitrite was oxidized to nitrate. Polyurethane strips proved to be better biomass support medium than cubes. Pseudomonas maltophilia and Pseudomonas putrefaciens were identified as denitrifiers in sludge. No clogging problems were observed during treatment of soft water. Denitrification of hard water resulted in clogging of the first reactor due to calcium carbonate sedimentation

One commercial plant, DENITROPUR, (Sulzer Company) using hydrogen has operated in Monchenglad bach, Germany since 1986 (Gros et al., 1988). The plant is designed to supply 100 m^3/h and reduce the nitrate concentration from 80 to 40 mg NO_3^-/L. Only part of the total water is denitrified and then mixed with raw ground water. A series of fixed beds, each filled with three dimensional corrugated elements acting as carriers are used for the biological denitrification. Pumped ground water is saturated with hydrogen gas before it is introduced into the biological reactors. Phosphate, carbonic acids and/or carbon dioxide are added. The denitrification reactor operated at a loading rate of 0.12 kg N/m^3-d, reduced the concentration from 75 to less than 1 mg NO_3^-/L. A sludge production rate of 0.2 kg organic matter/kg N was observed. The reproduction rate of autotrophic bacteria is low, therefore, less biomass sludge needs to be disposed. Reaeration, flocculation, filtration and ultravoilet disinfection are used as posttreatment. Back washing is required every 2-4 weeks. A denitrification rate of 0.25 kg N/m^3-d was reported. After five years of operations, results indicate that the treated water quality meets the German drinking water standards in all of

physicochemical. bacteriological and hygienic aspects. The treated water quality was reported to have nitrate < 1.0 mg N/L and nitrite < 0.01 mg N/L. The maximum nitrate - nitrogen removal rate are found to be 0 50 kg N/m^3-d and actual hydrogen consumption was about 11g per 100 g of nitrate (0 487 g per g N) as against a theoretical requirement of 0 35 g per g N (Rutten and Schnoor 1992)

2.2.3 Physicochemical Methods

While biochemical methods 'eliminate' the nitrate from water, separation and removal is the technique in physicochemical methods Physicochemical methods may broadly be divided in two classes

(i)   Membrane Separation.

(ii)   Ion exchange processes.

2.2.3.1 Membrane Separation

In the membrane separation processes, nitrates together with other water constituents (e.g. SO_4^{2-}, Cl^-, HCO_3^- etc.) are separated by passing the water through a semipermeable material. Reverse Osmosis and Electrodialysis are currently the two technologies being used in specific water purification systems. While the reverse osmosis is a pressure driven process. electrodialysis is electric potential driven. Reverse osmosis technology is unspecific and removes most of the dissolved solids, whereas electrodialysis selectively removes ions separating anions and cations. Reverse osmosis and electrodialysis were found to

effectively remove nitrate from drinking water (Rautenbach et al., 1986). These methods do not eliminate the nitrate, but produce a concentrated mass, which needs to be disposed of separately. The concentrated nitrate volume is about 10% of the total water production, with approximately 10-fold concentration of nitrate in it (Kruithof and Koppers. 1989). Because of the near total removal of constituent ions, to meet present standards, reverse osmosis is usually planned for a part of total well capacity and the treated and raw water is subsequently raised in proportion to give water of desired standads (Rautenbach et al., 1986). In contrast, electrodialysis system is normally designed for total water supply treatment, because operational conditions of low ion concentration are not economically justified for use of split treatment (Green and Shelef, 1994).

For reverse osmosis, a usable water recovery rate of about 75% is optimal (Bilyk and Szpadt, 1991). This is not acceptable when water resources are at a premium and brine disposal is economically objectionable. Under these constraints, the recovery rate should be at least 85%, requiring more expensive systems due to higher operating pressures, scaling, and reduced membrane lifetime. Even in the case of electrodialysis, where higher water recovery rates are possible, zero discharge is prohibitively expensive. Evaporation of concentrate may account for about 60% of the cost of water treatment (Rautenbach et al., 1986).

USEPA has identified reverse osmosis and electrodialysis alongwith ion-exchange as the "best available technologies" for nitrate removal, and water treatment costs for both of reverse osmosis and electrodialysis were reported to

be equivalent. Nitrate removal from ground water using reverse osmosis ranges from $ 1 55/m^3 treated in small systems to $ 0.40/m^3 treated in large systems, when nitrate concentration is reduced from 100 mg N/L to 10 mg N/L. Cost could be expected to be 20 - 50% lower if nitrate levels in raw water is about 50 mg N/L only (USEPA, 1991).

2.2.3.2 Ion Exchange Processes

Ion exchange processes are well established technology for water demineralisation for industrial applications, but in drinking water treatment it is a recent innovation (Clifford, 1990). It is considered to be the "best available technology" for nitrate removal together with reverse osmosis and electrodialysis (USEPA, 1991). Low installation costs and possibility of automatic control make ion exchange an attractive alternative for nitrate removal, especially for small facilities. According to Rogalla et al., (1990), installation cost of reverse osmosis is four times higher than the cost of heterotrophic biological dentrification and eight times higher than that of ion exchange.

In the ion exchange process, the nitrate ion is exchanged for either chloride or bicarbonate, depending on the resin used. Usually strong base anion (SBA) microporous resins are used with counter current or co-current regeneration in fixed beds or continuous systems. An anion exchange resin consists of a cross-linked polymer matrix to which charged functional groups are attached by covalent bonding. The usual matrix is polystyrene cross linked for structural stability with 3 to 8% divenyl benzene. The common functional group

falls into four categories: strongly acidic (e g. sulfonate. $-SO_3^-$); weakly acidic (e g. carboxylate, $-CO^-$), strongly basic (e.g. quaternuary amine, $-N(CH_3)_3^+$ and weakly basic (e g tertiary amine. $-N(CH_3)_2$). In anion exchange reactions with SBA resins. the quaternary amine functional exchange group $[-N(CH_3)_3^+]$ is so strongly basic that it is ionized and is therefore useful as an ion exchanger over the entire pH range of 1 to 13. Ion exchange of chloride for nitrate is currently the simplest and lowest cost option for removing nitrate from contaminated ground water to be used for drinking (Clifford. 1990). In France, since 1985. when five different resins were approved for drinking water treatment, 17 full scale water treatment plants using the ion exchange technique have been installed Three of these treat surface water, while all the rest fourteen are installed at ground water sources (Green and Shelef, 1994).

Typically ion exchange processes suffers from three difficulties. The main drawback of the process is the production of large amounts of waste with high concentration of nitrate, sulfate and chloride or bicarbonate concentrations, which are objectionable in direct disposal. Disposal of these concentrates can be problematic from both financial as well as environmental point of view.

The second problem in ion exchange process is of selectivity. A typical order of decreasing affinity in strong base anion (SBA) exchange resin is the following (Midkiff and Weber, 1970):

$$SO_4^{2-} > NO_3^- > Cl^- > HCO_3^-$$
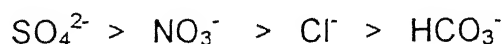
Thus a high sulfate concentration in raw water affects the nitrate removal efficiency The development of nitrate selective resins is an ongoing process. and is expected to improve the implementation feasibility of ion exchange technology for removal of nitrates from water containing high sulfate or chloride concentrations. The resins with a higher selectivity for nitrate can be produced by increasing the carbon atoms around ammonium nitrogen in the resin structure. The increasing order of ion selectivity for such resins changes to bicarbonate, chloride, sulfate, then nitrate. The nitrate to sulfate selectivity (K_s^N) increases from 100 to 1000 when ammonium nitrogen is surrounded by ethyl group in place of methyl groups (Guter, 1982). Clifford and Weber (1978) observed that sulfate selectivity can be reduced by increasing the distance between ion exchange sites, and nitrate selectivity can be increased by increasing the matrix and functional group hydrophobicity. The increased selectivity for nitrate has been attributed to steric strains in the resin that result from higher steric requirements of alkyl groups, and the higher capability of nitrate to reduce the steric strain over sulfate (Guter, 1982). Compared to trimethyl resins, triethyl amine resins increased the bed life by 62% when treating water containing 1.5 meq/L nitrate and 6.5 meq/L sulfate. Regenerant usage also decreased by 25-50%, thus reducing the operating cost. Use of nitrate selective resins reduce the nitrate 'dumping' or 'peaking' which occurs with conventional resins due to sulfate displacement of nitrate (Guter, 1982). Guter (1995) noted that as the alkyl groups increases in number of carbon in the chain, nitrate selectivity increases (e.g. trimethyl to tributyl increases selectivity by two

log units). Clifford et al., (1987) conducted a 15 month pilot scale study to evaluate nitrate removal from drinking water by ion exchange, reverse osmosis (RO) and electrodialysis (ED). The raw water contained 18-25 mg N/L, 43 mg/L sulfate, and 530 mg/L of total dissolved solids (TDS) All processes were able to reduce nitrate below 10 mg N/L. The ion exchange product water was high (500 mg/L) in TDS. Nitrate breakthrough always preceeded sulfate breakthrough and usually accompanied by a significant rise in pH. An increase in sulfate concentration from 42.5 to 310 mg/L in the feed water decreased nitrate breakthrough time from 400 to 180 bed volumes (BV). In successive use, the operation of ion exchange column in a partial regeneration mode (e.g. 60% nitrate elution) was found to be more economical than in a complete regeneration mode (e.g., > 95% nitrate elution) (Clifford and Liu, 1993).

Lauch and Guter (1986) reported that ion exchange process is approximately five times more economical than RO. Richard, (1989) noted that the capital investment for ion exchange plant can be 2.5-3.0 times less than that of a biological denitrification plant.

Another problem associated with the use of ion exchange technique for the removal of nitrates is the increase in both corrosiveness(due to chloride ions) and aggressiveness (low alkalinity) of water due to the replacement of nitrate, sulfate and bicarbonate ions (Richard, 1989). Correction of the treated water quality can add up to 10 - 20% of the nitrate removal costs (Rudd, 1989). These drawbacks can be avoided by using alternative regenerants, like sodium bicarbonate, but operating costs will be higher in that case. The carbon dioxide

regenerated ion exchange resins (CARIX process) for removing nitrate, sulfate, and hardness from water uses combined application of a weak-acid resin in free-acid form and an anion exchanger in bicarbonate form in a mixed bed. The exhausted exchange resins are regenerated through contact with a concentrated carbon dioxide solution. Wenli et al., (1994) indicated that carbon dioxide dissolution in water at a pressure of 5 - 5.5 bar produced an effective regenerate solution for optimum nitrate and hardness removal.

Among commercial ion exchange processes the 'CARIX' processes is designed for the combined reduction of hardness, nitrate and sulfate concentrations. Weak acid and bicarbonate are used as the cation and anion exchangers respectively. Both exchangers are used together in a mixed bed and are regenerated in one operation with carbon dioxide in counter flow mode. Since 1986, two full scale plants using the CARIX process for municipal water treatment have been installed in Germany and a third is expected soon (Green and Shelef, 1994). Bicarbonate (instead of carbon dioxide) is used in another full scale nitrate removal facility in South Staffordshire (England). This process consists of a two step counter-flow regeneration using brine followed by a conditioning bicarbonate stage to reduce chloride levels and to increase alkalinity in treated water. Sodium bicarbonate is generated on site itself by combining sodium hydroxide solution and carbon dioxide gas in a purpose-designed reactor. The plant is fully automated, controlled by a shophisticated computer system and operating as an unmanned facility (Fletcher et al., 1991)).

NITRACYCLE process, developed by the DEGREMONT Companies uses anion exchangers for nitrate removal from water. In France, six ground water NITRACYCLE treatment plants were built during 1986-1990 (Deguin et al., 1992). The Plouvenez - Lochrist (France) plant having a flows of 120 m^3/h uses Sodium chloride in counter current mode for regeneration. Reduction in regenerant consumption by recycling part of the regenerant has been applied in NITRACYCLE process.

The ECODENIT process, developed by OTV Company, uses ion exchange process with modified co-current mode of regeneration to reduce the regenerant consumption, which in turn reduce the amount of process water produced. Binic (France) plant with a design capacity of 160 m^3/h uses sodium chloride solution as a regenerant under modified co-current conditions (Philipot and Larminant, 1988).

The AZURION process, uses ion exchange for removal of nitrate and sodium chloride serves as regenerant under counter current mode. One such plant, at Ormes - Sur - Voulzie (France) with a flow of 27 m^3/h is under operation.

2.2.4 Physicobiological Methods

The main advantage of biological denitrification is that nitrate is selectively removed (eliminated) by its conversion to nitrogen gas with no waste concentrate produced except for a small biomass waste, which are easy to handle. The physico-chemical processes have the advantage of ease of operation. In a novel approach mostly first nitrate is removed from the water by using anion exchange

resins and the spent resin loaded with nitrate is regenerated by using bicarbonate or chloride. The eluant is treated by biological denitrification (Rittman and Huck, 1989). Manem (1993) reported a new generation of biological processes combining the advantages of both of physicochemical and biological processes. This class of treatment processes may be grouped as physico-biological processes.

A process combining membrane filtration and biological reactor is called Membrane Bioreactor (MBR). The new technology presents several advantages such as reliability, compactness, high loading rates and excellent effluent quality Ultrafiltration assures perfect disinfection of the effluent (Manem, 1993). The MBR process has been industrialised in March 1995 in Douchy, France, and produces 400 m^3/d of potable water that is denitrified, disinfected (due to ultrafiltration), and free from pesticides and organic matter. The process known as BIOCRYSTAL is an adaptation of MBR technology that includes powdered activated carbon (PAC) addition in a way similar to that of CRYSTAL process, developed by Lyonnaise des Eaux a few years ago (Urbain et al., 1996). A similar approach is followed in the denitrification by entrapped mixed microbial cells immobilization (EMMCI) process. The mixed microbes are entrapped into - polymeric cellulose triacetate. Nitisoravut and Yang (1992) operated one such reactor for more than one year with feed concentration ranging from 50 - 850 mg .N/L and hydraulic retention time (HRT) of 1.80 to 11.30h. Complete denitrification was reported to be obtained at an HRT of 2.60 - 11.30h. At an HRT of 1.80h, the maximum nitrate - nitrogen loading rate of 591.60 g/m^3h (based on

carrier volume) was achieved with an 88.3% denitrification efficiency. Under high range of sodium bicarbonate concentration in the range 10,000 - 20,000 mg/L, denitrification efficiency more than 96% could be obtained. Thus, EMMCI process is claimed to give very promising results for nitrate removal. Lin and Chen (1995) reports another such investigation of denitrification and methanogenesis in a mixed culture system coimmobilized in a polyvinyl alcohol (PVA) gel beads. The coimmobilized system is claimed to have solved the problems of noncompatibility of denitrifiers and methogens present in a suspended mixed culture system. The application of such a process should not only achieve an effluent quality of low levels of nitrate and organics, but also possibly eliminate the necessity of post treatment to remove the organic residuals in the denitrified effluent (Lin and Chen, 1995).

2.3 ION EXCHANGE RESINS AND INORGANIC ION EXCHANGERS

Ion exchange is a widely applied process for industrial water treatment, but health considerations regarding the release of undesirable substances by the synthetic resins had initially slowed the application of this technology (Philipot and Patte, 1982) to the particular field of drinking water treatment. Initially the matrix for ion exchange materials used to be polystyrene cross linked with divenyl benzene for structural stability. Strongly basic anion resins based on an acrylic polymer claims the advantage of greater resistance to organic fouling over styrene based resins. Biswas and Packirisamy (1985) have given a thorough discussion on the different synthetic ion exchange resins. Dore, et al.,

(1986) examined the quality of water treated by a SBA resin regenerated with brine. The constituent monomers leached from resin were styrene, divinylbenzene, trimethylamine. and their derivatives. Conditioning by NaOH, distilled water, a HCl solution, and distilled water eliminated the majority of leachable constituent monomers and the ion exchange process was shown not to contribute toxic organic chemicals to treated water. Flemming (1988) reported the tendencies to avoid the use of resin based ion exchangers in special field of water treatment because of the risk of bacterial contamination by the ion exchange units. Anion exchange resins, which is used for nitrate removal from water has other serious limitation also.

Ball and Harries (1988) reported that anion exchange resins are less stable than cation exchange resins and undergo a degradation of the exchange group in service. Strongly basic groups of anion exchange resins undergo thermal degradation over 20-80^{0}C, with a consequent loss of capacity. They are also more susceptible to foulants, particularly natural organic compounds, which can affect performance. In such situations,synthetic inorganic ion exchangers appear to be a suitable alternative, particularly for drinking water treatments. A large number of synthetic inorganic substances has been described which exhibit ion exchanging properties.

Hydrous oxide and acidic salts of multivalent metals have been the most intensively studied groups of synthetic inorganic ion exchangers. The adsorptive properties of hydrous oxides such as alumina, silica and ferric oxide have been known for many years and it has been established that the adsorption of ions by

them is presumably by ion exchange (Vesely and Pekarek, 1972). Hydrous oxides are of particular interest because most of them can function both as cation and anion exchangers, and under certain conditions, both cation and anion exchange can occur simultaneously. However, a review of literature concerning anion exchange properties of these hydrous metal oxides reveals, that either nitrate ion has not been studied thoroughly or very few of the reported materials have shown nitrate uptake properties. Hydrated alumina showed a slight preference of Cl^- over NO_3^- (Abe and Ito, 1965) and saturation capacity for anions increased with decreasing pH. Among quadrivalent elements, zirconium oxide behaves both as cation and anion exchangers, with point of zero charge (pH_{pzc}) at pH = 6.5 (Vesely and Pekarek, 1972). The equilibrium constants for the exchange of anions show a slightly higher selectivity towards chloride as compared to nitrate and it is very selective towards phosphate ion. Most of the quinquevalent and sexivalent hydrous metal oxides show cation exchange properties. Hydrous Nb_2O_5 acts both as cation and anion exchanger and is selective towards $Cr_2O_7^-$ and ferrocynides. Acidic salts of multivalent metals mostly acts as cation exchangers due to the presence of readily exchangeable hydrogen ions (Vesely and Pekarek, 1972).

A survey of available literature suggests that among inorganic ion exchange materials in general, and hydrous metal oxide and acidic salts of multivalent metals in particular, very little information is available which can beneficially be used for nitrate removal from water to be used for drinking purposes. Fritsche (1993) has reported the use of wet yellow bismuth hydroxide

precipitate for removal of nitrate (and other anions) from water. Hence it appears imperative to investigate and assess bismuth compounds for their potentials to remove nitrate from water and its possible applications in drinking water treatments.

2.4 BISMUTH

Bismuth displays valencies of -3, +3 and +5. In the hydride, BiH_3, bismuth has a valency of -3. The compounds of Bi (III) are the most important ones in analytical chemistry. The compounds of bismuth (V)-alkali metal bismuthates-are known only in the solid state. The ions of bismuth (V) do not exist in solution (Bhatki, 1977).

Bismuth exists in aqueous solutions as Bi (III). Unless bismuth solutions are kept rather strongly acidic, they are susceptible to hydrolysis even at pH values 1-2, forming insoluble basic salts. The action of water on any of the bismuth trihalide, nitrate or sulfate produce insoluble bismuthyl precipitates These precipitates are non-hygroscopic.

2.4.1 Bismuth and Nitrate in Aquous Environment

There is considerable evidence for the association of Bi (III) and nitrate ions in both aqueous solutions and solids (Ortel and Plane. 1968). All bismuth nitrate salts rapidly hydrolyse to give basic bismuth nitrates. The *bismuticum subnitricum, bismuth subnitrate,* the *magisterium bismuti, magistery of bismuth, basic bismuth nitrate, bismuth-white, pearl-white, blanc d' expagne, spanish white,* and white cosmetic are pharmaceutical or trade names for the basic nitrate

or mixture of basic nitrates obtained by adding water to bismuth nitrate (Mellor. 1957). Several other white powders were also called Spanish-white or pearl-white The composition of white precipitate depends on the temperature and on the proportion of water employed.

2.4.2 Pharmacology and Toxicology of Bismuth

As an element, bismuth is one of the least toxic of the heavy metals and cases of bismuth poisoning in industrial use have not been recorded. Therefore. toxicity is not a problem in the handling of bismuth (Howe, 1968).

(a) Pharmacology:

Bismuth and its compounds have traditionally been widely used in medicine and veterinary practice. Finely divided bismuth was injected intramuscularly as an aqueous suspension in treatment of syphilis and yaws. Its advantage was the slow adsorption, possibly as protein bound complex, giving continuous therapeutic action (Wilkinson, 1987). Bismuth nitrate (magisterium 'bismuti'), a white pigment was used in beauticare, painting and as a medicant in the 17th century. In this century, various bismuth salts have been used to treat syphilis, as antihypertensive, as diureteics and for the treatment of gastrointestinal disorders. Bismuth is used as K_3 [Bi (III) (citrate)] in De-Nol (a commercial medicine) which is used as Antacid and/or antiulcer. Colloidal bismuth (III) subcitrate is available for the treatment of peptic ulcers and bismuth subgallate and oxide are used as skin antisceptics (Sadler, 1991).

(b) Toxicology:

For bismuth, the toxic problems which have been recorded have in the main been diatrogenic illness i.e. diseases produced by doctors as a side effect of pharmacology The effect of acute bismuth intoxication include gastrointestinal disturbances, anoxia, headache, malouse, skin reactions, discoloration of the mucus membranes and mild jaundice (Wilkinson, 1987). A characteristic blue-black line on the gum, the "bism uth-line", which may persist for years is a feature of bismuth overdosage Soluble salts are excreted via urine and may cause mild kidney damage. Less soluble salts may be excreted in the faeces, which may be black in color due to the presence of bismuth sulfide. Table 2.2 contains some toxicity data of bismuth and its related compounds (Wilkinson, 1987).

Table 2.2

Pharmacology and Toxicology of Bismuth Compounds

Compound	Mammal	LD_{50} (mg/kg)	LD_{10} (mg/kg)	Method of Adm ission
Bi metal	Man	-	221	Not stated
BiOC1	Rat	22	-	Not stated
$Bi(NO_3)_3$	Mouse	-	21	Intravenous
$Bi(NO_3)_3$	Mouse	-	2500	intraperitoneal

2.4.3 Sorptive Properties of Bismuth Compounds

Many bismuth compounds have been shown to have sorption/ion

exchange properties. Krause and Nelson (1956) used the "mixed oxides of bismuth" and found high selectivity of chloride ion in neutral solutions. In 1960, the United Kingdom Atomic Energy Authority patented a method for recovery of plutonium (as anionic complex) from uranium and/or fission products using bismuth hydroxides. Ito and Yashida (1970) used bismuth hydroxide, $Bi(OH)_3$ for adsorption of chloride at a level of 0.1N HCl. Anand and Baxi (1978a, 1978b) used basic bismuth nitrate and basic bismuth silicate as an (ion) exchange material for various anions such as Cl^-, Br^-, I^-, SO_4^{2-}, HPO_3^-, PO_4^{3-} and $Cr_2O_7^-$ at 0.1N level in sodium salt form. Kodama (1993) developed a new inorganic anion exchanger from thermal decomposition of basic bismuth nitrate and used it to remove iodide for conc. <2.0 moles/L. Thus, bismuth compounds appear to have definite sorptive properties which can beneficially be used in water contaminant removal.

CHAPTER 3

SCOPE OF THE PRESENT STUDY

Nitrate contamination of water resources is a serious concern in many part of the world. Ground water, which is a major source of drinking water in India and most of the developing countries is worst affected by nitrate pollution. Development and evaluation of nitrate removal techniques for drinking water purification has been identified as a priority item for a number of national and international environmental programmes. Since, economic considerations often do not permit community water treatment plants, point-of-use home purification devices appear promising. In this respect, ion exchanger using carbon based resins is presently a widely accepted option for nitrate removal Comparative studies on ion exchangers have revealed that anion exchange resins are less stable than cation exchange resins and undergo degradation of the exchange group in service. They are also more susceptible to foulants, particularly natural organic compounds, which can affect the performance (Ball and Harries, 1988). There are reports of avoiding resin based ion exchangers in home water purification because of possible release of undesirable organic substances in the treated water. Bacterial contamination of the resin units has also been observed (Flemming, 1988).

These observations suggest a search for inorganic media for drinking water treatment. Fritsche (1993) observed removal of nitrate and other anions from water using wet precipitate of yellow bismuth hydroxide. Many compounds of bismuth are in public use in beauticare and medicinal applications. In aquous environment, sorptive and anion exchange properties of "mixed oxides" of bismuth (Krause and Nelson, 1956), bismuth hydroxide (Ito and Yashida, 1970), basic bismuth nitrate (Anand and Baxi, 1978a, Kodama, 1993) have been reported. The literature information on nitrate removal using bismuth based media is still scanty.

The objective of the present study was to develop and assess bismuth based inorganic media for nitrate removal from water with a view to use them in home water purification systems. The study was undertaken along the following lines:

(i)   Identification of promising bismuth compounds in terms of nitrate removal from water.

(ii)   Preparation and characterization of the selected material (s).

(iii)   Elucidation of possible mechanisms of nitrate removal.

(iv)   Evaluation of regeneration and reuse potential of the material (s).

(v)   Effect of other competing anions, such as chloride, bicarbonate and sulfate on nitrate removal.

(vi)   Evaluation of the selected material in nitrate removal from ground water.

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIALS

4.1.1 Glassware and Plastic Bottles

All glassware used in the present study were manufactured by M/S Borosil Glass Works Ltd., Bombay, marketed under the brand name `Corning' and `Borosil'. For batch exp eriments, plastic bottles of 300 mL capacity, marketed under the brand name of TARSON INDIA, were used. Before use, all of them were washed with liquid soap, labwash (M/S Sarabhai M Chemicals, Baroda), followed by tap water washing and a final rinse with distilled water.

4.1.2 Water

Laboratory distilled water further distilled twice in a glass distillation plant (M/S Vensil Glass Works. Pvt. Ltd., Banglore) was used in all batch sorption experiments. This triple distilled water (TDW) showed an average pH of 7.0 and conductivity less than 2 micro siemens/cm. For large scale washing and continuous flow system, laboratory distilled water (DW) was used. The pH of laboratory distilled water averaged around 6.8. In the later phase, for evaluation of the selected medium in nitrate removal, ground water was used to prepare the

feed solution for column studies. Characteristics of the ground water employed are given in Table 4.1.

TABLE 4.1

Characteristics of I.I.T Kanpur Ground Water

Parameter	Value/Range
Turbidity	Not detectable
pH	8.0 - 8.2
Conductivity	840 – 1100 micro siemens/cm
Total Alkalinity	415 – 450 mg $CaCO_3$/L
Total Hardness	190 – 200 mg $CaCO_3$/L
Chloride	32.0 mg/L
Sulfate	42.0 mg/L

4.1.3 Chemicals

All chemicals used in the investigation were of analytical reagent (AR) grade. Stock nitrate and chloride solutions were prepared using their respective potassium salt. Sodium bicarbonate was used for all alkalinity preparations.

4.2 METHODS

4.2.1 Determination of Nitrate Concentration

Nitrate concentration in water was determined using, ion-meter (Micro-2), manufactured by Toshniwal Process Instruments Pvt. Ltd., Ajmer (India), with nitrate ion selective electrode (ISE 311). Distilled water based nitrate standards were used to calibrate the instrument before sample tests. Potassium

4.2.3.2 Sorption Equilibria

Sorption equilibria were conducted to determine the nature of isotherm for 24h contact time. For this set of experiments, nitrate concentration ranged between 0.5 to 10.0 meq/L and a sorbent dosage of 40.0 g/L was used with each sample.

4.2.3.3 Sorption Kinetics

Kinetic studies were conducted for the selected media at 1 meq/L nitrate level. The reaction mixture consisted of a 100 mL of nitrate solution with 40 g/L of sorbent. The contact time ranged between 15-240 min. and the contents were agitated in end to end rotatory shaker at 20 rpm. Samples were withdrawn from the shaker at the end of the desired contact time and the filtrate through the Whatman 42 filter paper was analysed for remaining nitrate concentration.

4.2.4 Column Tests

The performance of media was evaluated in (60 cm long), 2.50 cm internal diameter (ID), cylindrical columns. The columns were fitted with perforated glass at the base. In order to retain the fine media particles without loss, 5.0 g of acid washed (0.1N, 24h) sand (250 μm $\leq$ d $\leq$ 425 μm) was used in each column to provide an uniform bed beneath the medium. All columns were run in downflow mode and a constant static head of about 2.0 m was maintained in all the experiments. Sufficient distilled water was passed through beds to

clean the washable impurities before applying the desired feed solution and all changes in feed solution were preceeded by a similar thorough in-situ distilled water washing of the medium.

4.3 MEDIA PREPARATION AND CHARACTERIZATION

4.3.1 Preparation

For screening, bismuth compounds in the form of oxide. hydroxide, oxychloride and carbonate were evaluated for their potential to remove nitrate from water. Wherever required bismuth trioxide (Bi_2O_3, MW = 466 0) powder of commercial AR grade was used without further purification. In order to keep uniformity, a 0.1M Bi_2O_3 solution in 2N HCl was used in all other preparations.

Bismuth hydroxide. in the form of yellow precipitate was prepared using the method described by Fritsche (1993). For this. the 0.1M Bi_2O_3 solution was mixed with three times of its volume of 2N NaOH. After a reaction time of 1h, the precipitate was separated from the liquid by filtering through a coarse cotton cloth and washed with sufficient distilled water to remove all free hydroxide and chloride. Finally the washed and filtered precipitate was dried at 103 ± 2° C for 24h to give powder form of the medium.

Bismuth oxychloride powder was obtained using the method similar to Schulten (1900). In this. the working 0.1M Bi_2O_3 solution was allowed to hydrolyse in ten times of its volume of distilled water for 24h. The white precipitate was then decanted out and washed with sufficient distilled water to

remove all unreacted acid or chloride Finally, the precipitate was dried at 103 ± 2^0C for 24h, as suggested by Bhatki (1977).

Normal carbonate being unknown, bismuthyl carbonate, $(BiO)_2CO_3$, is the only carbonate compound of bismuth (Parkes, 1959). This was prepared by mixing the working 0.1M Bi_2O_3 solution with three times the volume of 2N sodium carbonate solution. After a reaction time of 1h, the precipitate was decanted out, washed with sufficient distilled water to remove all unreacted chemicals and finally dried at 103 ± 2^0Cfor 24h.

In order to study the formation of yellow bismuth hydroxide. four forms of hydrous bismuth oxides (HBOs) were prepared by mixing the working solution of 0.1M Bi_2O_3 in 2N HCl with increasing volumetric proportions of 1:1. 1:2, 1:3 and 1:4 of 2NNaOH. The precipitates obtained were washed with sufficient distilled water to remove all unreacted impurities and finally after filtering through Whatman 42 filter papers. were dried at 103 ± 2^0C for 24h. The powders so obtained were designated as HBO (1), HBO (2), HBO (3) and HBO (4) respectively.

4.3.2 Characterization

4.3.2.1 Specific gravity of HBO Powders

Specific gravity of a dry HBO powder was estimated using water displacement technique, similar to the one used for determination of specific gravity of sludge, as per Standard Methods (1985). In this, a clean dry 50 mL

volumetric flask was first weigh ed (1). Then nearly 5.0 g of dry powder was taken and the flask was weighed again in stoppered condition (2). Distilled water was then slowly poured into the flask to about half of it. The contents of flask was slowly heated to near boiling temperature in order to expel all entrapped air from the powder. The flask was then cooled to room temperature and filled with distilled water and stoppered tightly such that no air bubbleremained entrapped inside. Weight of flask along with powder and water was taken(3) Finally, the flask was emptied and filled with distilled water alone. The weight of stoppered flask was again recorded (4).

Specific gravity of powder = Weight of powder / Weight of equal volume of water at 4^0C

$$= \{(2) - (1)\} / [\{(4) - (1)\} - \{(3) - (2)\}] \times F$$

where F is the temperature correction factor (= 0.9975 at 25^0C).

4.3.2.2 pH of Point of Zero Charge (pH$_{pzc}$)

The pH of point of zero charge (pH$_{pzc}$) of powders were estimated by the fast alkalimetric titration method (Huang and Ostovic, 1978). To each of four 100 mL identical portions of 10^{-1}, 10^{-2} or 10^{-3} M solution of NaCl, 1.0 g of powder was added. Following a 12h agitation in an end to end shaker at 20 rpm. one portion was titrated in presence of the powder with 0.1N HCl and other with 0.1N

NaOH. Volume of acid or alkali consumed corresponding to each pH difference of 0 50 unit was recorded. The other two portions were allowed to settle and the solid materials were separated by filtering the contents through Whatman 42 filter paper. The filtrates were titrated similarly. The net titration curve for each ionic strength was obtained by subtracting the titration curve of the filtrate samples from that of the portion with powder. In absence of specific chemical interaction between the single electrolyte and the surface of sorbent, the net titration curves 'usually' meet at a point, that is defined as pH_{pzc} (Huang, 1977).

CHAPTER 5

RESULTS AND DISCUSSION

In view of the investigative nature of the study, experimental works were carried out in several phases, each phase with its own set of objectives. Selecting a medium preferably in the dry form, which can remove nitrate from water and the search for the possible mechanism behind the removal remained the ultimate objective of the study. Experimental results are presented in graphical, bar chart or tabular form as suitable. For most part, only typical results have been shown. Most of the experiments were conducted at a nitrate contamination level of 1 meq/L (= 14.0 mg N/L or 62.0 mg NO_3^-/L). In the last phase of the study, the selected medium was tested with 1 and 2 meq/L of nitrate in ground water. A discussion of the result follows each phase of the experimental work.

5.1 IDENTIFICATION OF PROMISING MEDIA AND FACTORS AFFECTING NITRATE REMOVAL

5.1.1 Screening Of Potential Compounds

Powders of bismuth trioxide, bismuth oxychloride, bismuth carbonate, and yellow bismuth hydroxide, were used for screening tests. Results of batch sorption test are shown in Fig. 5.1. It is observed that while bismuth trioxide and
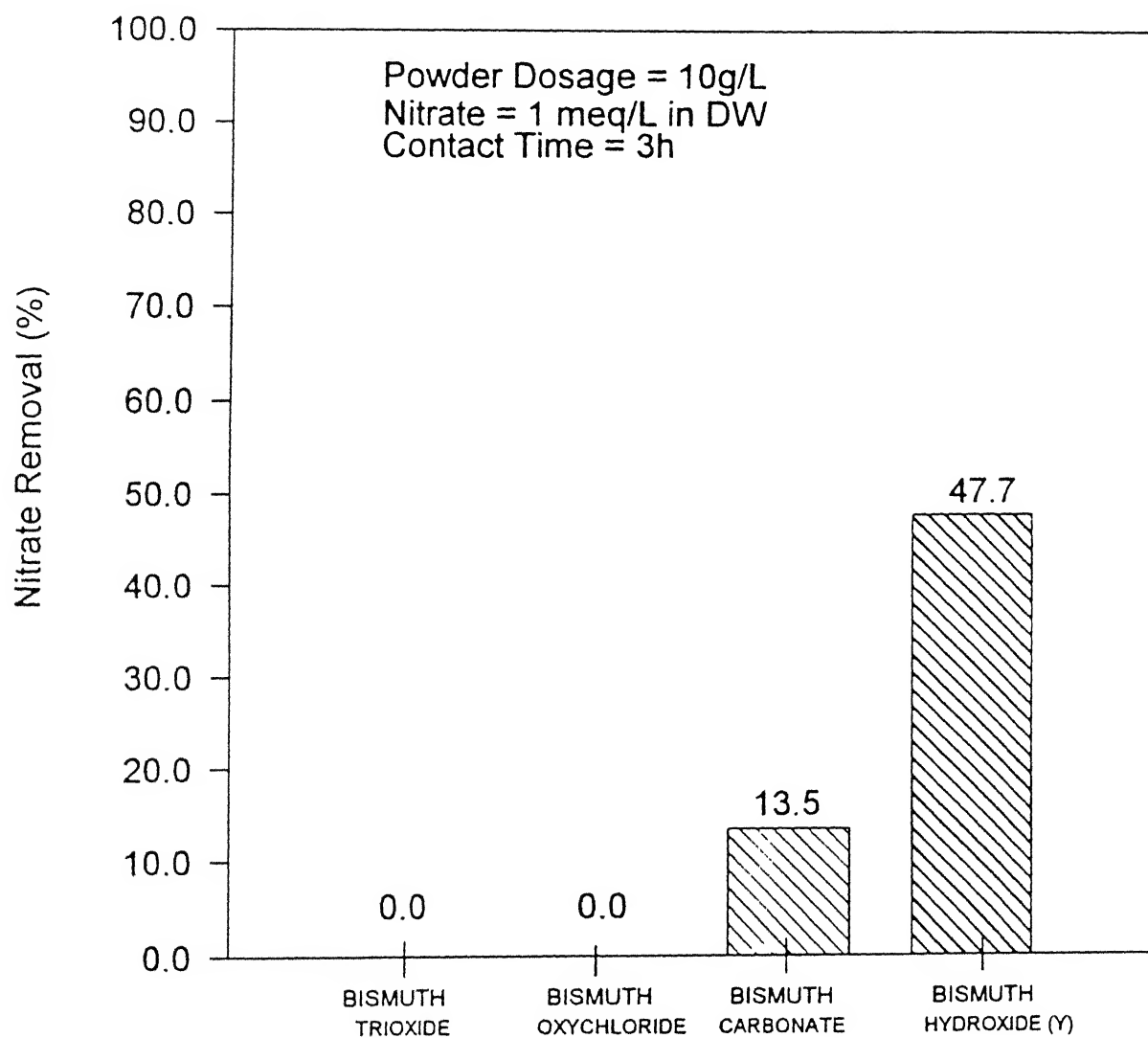
Fig. 5.1 Nitrate Removal by Potential Compounds

bismuth oxychloride did not show any appreciable nitrate sorption (removal), bismuth carbonate and yellow bismuth hydroxide gave 13.5 and 47.7% removals at 1 meq/L nitrate level.

In aquous solutions, behaviour of metal oxides are also similar to hydrous metal oxides (HMOs), because their surface chemistry invariably reveals that they are atleast partially hydrated (Kinniburgh and Jackson, 1981). Anand and Baxi (1978a) also reported rehydrolysis and anion exchange properties of Bi_2O_3, obtained from decompo sition of basic bismuth nitrate at 550°C. It appears that whereas Bi_2O_3 obtained from basic bismuth nitrate might contain some exchangeable anion, pure Bi_2O_3 (AR grade, as used in this experiment) lacks such characteristics and hence does not show such behaviour.

Bismuthyl compounds are formed from univalent $[Bi = O]^+$ or $[Bi \rightarrow O]^+$ radicals and there is no indication that they ever go in covalent form (Sidwick, 1950). Under suitable conditions, nitrate can be exchanged with chloride. Bismuth oxychloride, however, didnot show nitrate removal to any observable extent. Possibly chloride in the compound, as prepared by this method, is not suitably free for exchange with nitrate at this concentration Bismuthyl carbonate, $(BiO)_2CO_3$ is the only known carbonate compound of bismuth. In absence of bicarbonate ions (which can exchange nitrate), it appears that small nitrate removal by bismuth carbonate is by physiosorption. Bismuth hydroxide. which is yellow in color gave the highest nitrate removal among all tested compounds Theoretically a monomeric BiOOH compound should be colorless, as $[BiO]^+$ ion is colorless (Muylder and Pourbaix, 1966). Hollemann and Wiberg (1960) also

reported yellow bismuth hydroxide to be "presumably" polymeric. It is to be noted that yellow bismuth hydroxide is formed under presence of excessive hydroxide. In case of hydrous ferric oxide precipitate also, polymerisation is accelerated by a higher hydroxide ion concentration and elevated temperature (Stumm and Morgan, 1962; Matijevic et al., 1975). Thus, it appears that yellow bismuth hydroxide is a polymeric form of bismuthyl hydroxide, BiOOH. Whereas pH of bismuth oxychloride and bismuth carbonate treated water showed slight decrease than the initial pH, those with bismuth trioxide and yellow bismuth hydroxide remained almost on similar levels of initial solution. This indicates that in polymeric bismuthyl hydroxide, hydroxyl ions are not suitably free for nitrate exchange.

5.1.2 Temperature of Drying of Media

A dry form of sorbent is desirable because of practical considerations, but the method of dehydration affects many properties of the material including granularity and ion exchange capacity. As reported earlier, organic anion exchange resins having strongly basic groups undergo thermal degradation over 20-80^{0}C, with consequent loss of capacity (Ball and Harries, 1988). Hydrous metal oxides and ion exchange resins both are water swollen gels. Hydrous oxides of chromium(III), zirconium(IV), tin(IV) and thorium, to be used as ion exchangers are dried at room temperature (Reiman and Walton, 1970). For reproducible properties, however, a defined temperature of drying needs to be ascertained. Both of bismuthous hydroxide, $Bi(OH)_3$ and bismuthyl hydroxide,

BiOOH are written in their hydrated forms interchangeably. Although Krause et al (1935) distinguished between "true hydroxide" and hydrated oxide and categorized bismuth hydroxide (presumably $Bi(OH)_3$), as "true hydroxide", bismuthous hydroxide, $Bi(OH)_3$ is still written as $Bi_2O_3 .3H_2 O$ (Gmelins, 1964; Muylder and Pourbaix, 1966) and bismuthyl hydroxide, BiOOH, as $Bi_2O_3. H_2O$ (Gmelins, 1964). $Bi(OH)_3$ or $Bi_2O_3. 3 H_2O$ is amorphous and white in color (Muylder and Pourbaix. 1966). It loses water continuously on rising temperatures, hence, it is dried at room temperatures (Remy, 1956). However, when the precipitate obtained in usual manner is dried at 100^0C, its composition approximates to BiOOH (Remy, 1956; Durrant and Durrant. 1962). Corfield and Woodword (1924), when heating the $Bi(OH)_3$, found that, the composition approximates to $Bi_2O_3 1.5 H_2O$ at 100^0C. As noted by Levin and Roth (1964), John de Groot at National Bureau of Standards Laboratory dried bismuth oxyhydroxide BiOOH, at 60^0C for 17 h and then at 85^0C for 65 h. As BiOOH is a stronger base than $Bi(OH)_3$ (Mellor, 1957) and may be more effective in anion exchange, a drying temperature of 103 ± 2^0C appears the most suitable for hydrous bismuth oxides (HBOs). This should also reduce any further thermal degradation of material in the working environment.

5.1.3 Effect of pH on Nirate Removal by Yellow Bismuth Hydroxide

As yellow bismuth hydroxide performed the best in nitrate removal, it was selected for pH effect studies. In order to check whether removal of nitrate improves on decreasing influent pH, batch sorption experiments with different

initial pH ranging between 3 and 9 were conducted with yellow bismuth hydroxide powder. The results are shown in Fig. 5.2. As such, it appears that there is no significant change in nitrate removal due to change in initial pH of solution within the observed range. Thus, it seems that within this range pH is not a very sensitive parameter for nitrate removal by yellow bismuth hydroxide powder

5.1.4 Nitrate Removal by Hydrous Bismuth Oxide (HBO) Powders

The preparative conditions of yellow bismuth hydroxide are such that it requires large volume of distilled water for washing the unreacted hydroxide. Even a small presence of free hydroxide with powder may increase the pH of water well above 10 in distilled water systems. Removal of unreacted hydroxide in the form of ammonium hydroxide (NH_4OH) is relatively easy, particularly while drying at higher temperatures, but even the most concentrated ammonium hydroxide (Specific gravity = 0.91, Assay = 25%) failed to produce yellow bismuth hydroxide with working solution of Bi_2O_3. The powder obtained from using ammonium hydroxide was visibly white and removed only 25.6% nitrate from water under similar conditions of experiment as against 47.7% observed for yellow bismuth hydroxide at 1 meq/L influent level. In order to check whether the use of sodium hydroxide itself can be reduced in preparing the bismuth hydroxide following a method similar to Fritsche (1993), three hydrous bismuth oxides (HBOs), designated as HBO(1), HBO(2) and HBO(3), were prepared from a 0.1 M Bi_2O_3 solution in 2N HCl with successively increasing volumetric ratio of
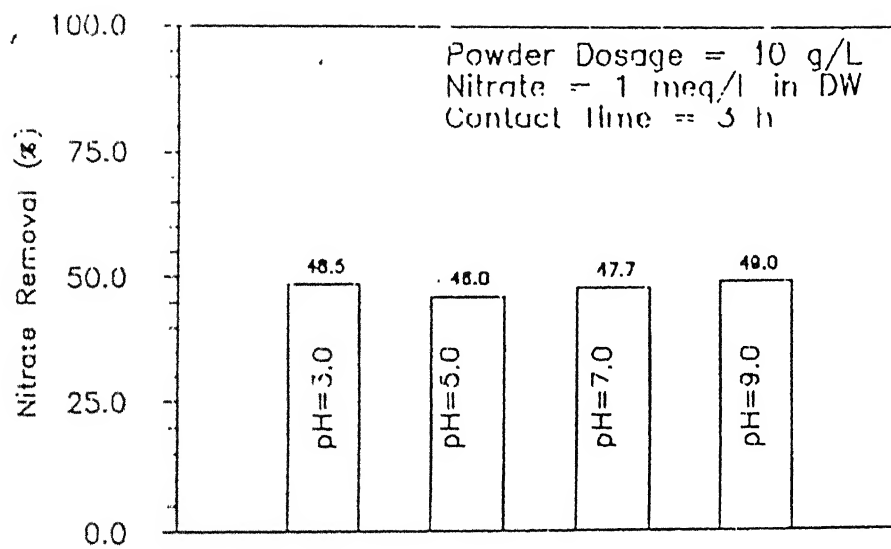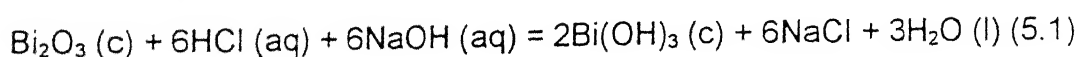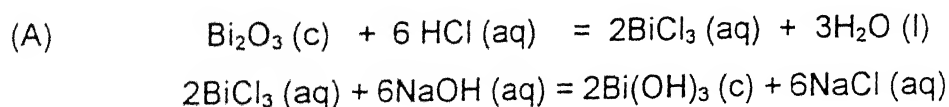
Fig. 5.2 Effect of pH on Nitrate Removal by Yellow Bismuth Hydroxide.

1 1, 1 2 and 1:3 of 2N NaOH respectively. The obtained precipitates were similarly washed for unreacted chemicals and dried at $103\pm2°C$. Whereas HBO(1) was visibly white. HBO(2) and HBO(3) were predominently yellow in color. In order to distinguish the two yellow HBOs from pure Bi_2O_3 powder, bismuth trioxide itself was also included in nitrate sorption tests. Powder dosage of 40 g/L were used for a contact time of 24h at 1 meq/L nitrate level in distilled water The results are shown in Fig. 5.3. It is observed that whereas Bi_2O_3 powder and HBO(1) are poor in nitrate sorption, giving only 5.7 and 16.0% removals. both HBO(2) and HBO(3) show almost similar performances, giving 81.6 and 81 7% of nitrate removal respectively. Thus, it appears that both yellow hydrous bismuth oxides. HBO(2) and HBO(3) are similar in nitrate removal performances. However, they are significantly different from Bi_2O_3 powder as far as nitrate removal is concerned. The final pH of solutions showed no significant changes with Bi_2O_3, HBO(2) and HBO(3). However, some decrease in pH with HBO(1) was observed.

Based on purely theoretical consideration and assuming monomeric compound formation, hydrochloric acid solution of Bi_2O_3 may produce two forms of bismuth hydroxide :

(A) $\quad\quad Bi_2O_3$ (c) + 6 HCl (aq) = $2BiCl_3$ (aq) + $3H_2O$ (l)

$\quad\quad\quad 2BiCl_3$ (aq) + 6NaOH (aq) = $2Bi(OH)_3$ (c) + 6NaCl (aq)

$\quad\quad Bi_2O_3$ (c) + 6HCl (aq) + 6NaOH (aq) = $2Bi(OH)_3$ (c) + 6NaCl + $3H_2O$ (l) (5.1)

$\Delta G_f° - 118.55 - 31.37 \quad\quad -99.23 \quad\quad - 138.55 \quad\quad -91.78 \ - 56.68$

Fig. 5.3 Nitrate Removal by Hydrous Bismuth Oxide Powders

and (B) $\quad Bi_2O_3$ (c) $+$ 6 HCl (aq) $=$ $2BiCl_3$ (aq) $+$ $3H_2O$ (l)

$\quad\quad 2BiCl_3$ (aq) $+$ 6NaOH (aq) $=$ 2BiOOH $+$ 6NaCl (aq) $+$ $2H_2O$

$\quad Bi_2O_3$ (c) $+$ 6HCl (aq) $+$ 6NaOH (aq) $=$ 2BiOOH (c) $+$ 6NaCl $+$ $5H_2O$ (l) (5 2)
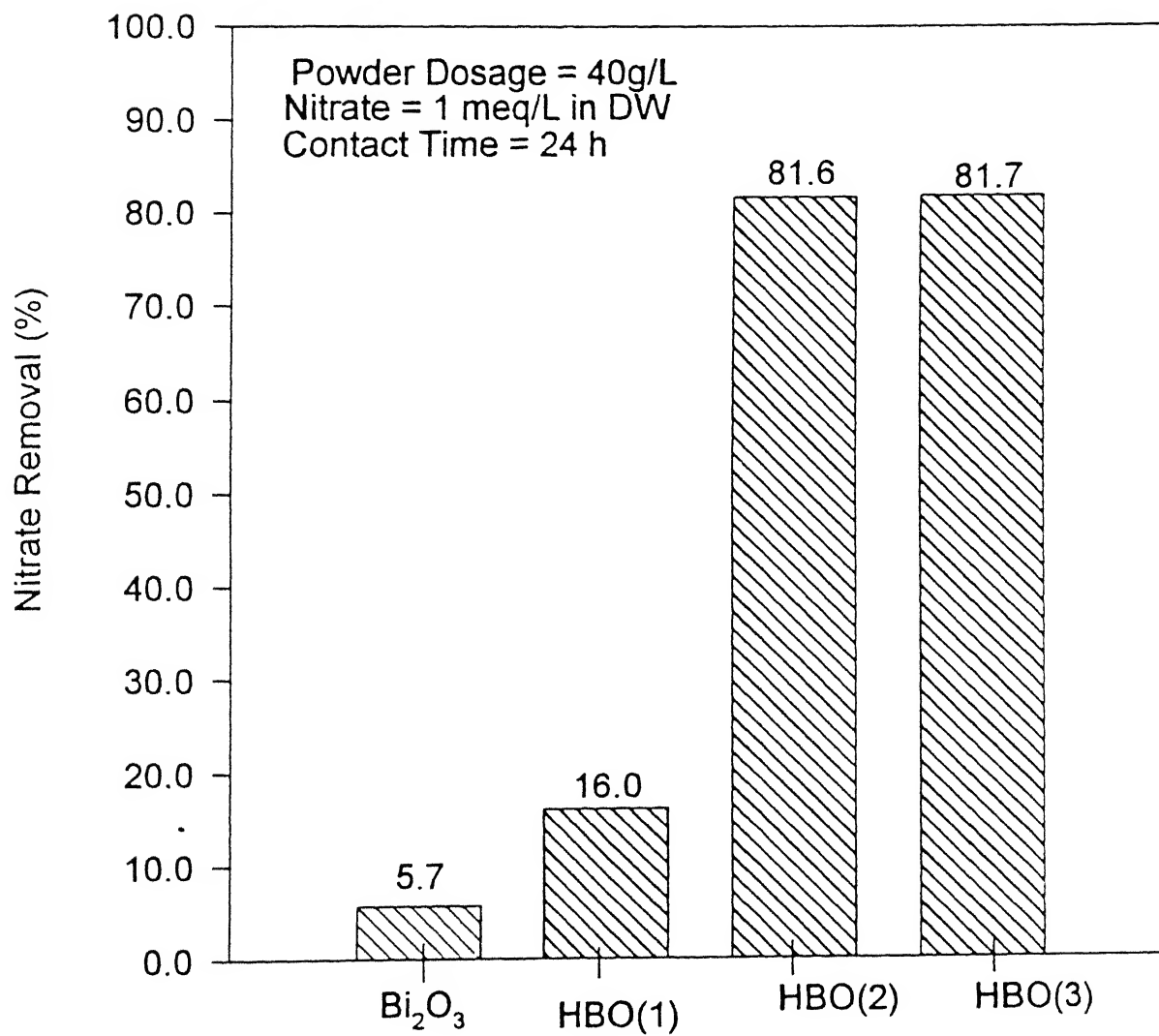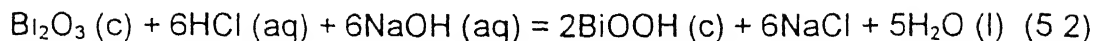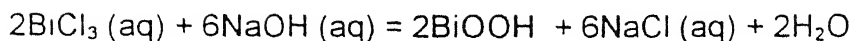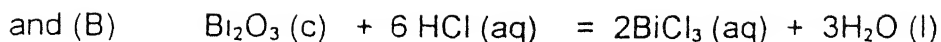
ΔG_f° - 118.55 -31.37 $\quad\quad$ -99.23 $\quad\quad\quad$ -88.4 $\quad\quad\quad$ -91.78 - 56 68

where ΔG_f° is the Gibb's free energy of formation (kcal/mole) under standard state conditions.

The Gibb's free energy of reaction for equation 5.1 and 5.2 are -95.67 and -108.73 kcal respectively. Hence both the reactions seem feasible, but bismuthyl hydroxide, BiOOH should be the ultimate product of reactions.

It is interesting to note that formation of both the forms of bismuth hydroxide in their monomeric form require an acid to alkali ratio of 1:1 only, as is evident from equations 5.1 and 5.2: HBO (1) has been prepared using an acid (solution of Bi_2O_3) to alkali ratio of 1:1 and hence, as a final product, HBO (1) is white which is in line with the theoretical prediction for monomeric BiOOH.

The color of a substance is determined by its absorption spectrum and all colorless ions have absorption bands in ultravoilet range (Pauling, 1960). However, if through a perturbing influence, like formation of a bond with increasingly great covalent character, a single absorption band of an ion were increased in wave length, so as to pass through the visible spectrum, the color of the ion by transmitted light would go through the sequence of lemon yellow, yellow, orange, red, purple and so on. Thus, this sequence of color may be used as a measure of the amount of covalent character of compounds with colorless ions (Pauling, 1960). It appears that HBO (2) and HBO (3) which are yellow in

color and are formed under the presence of excess hydroxide ions are polymeric forms of bismuthyl hydroxide, BiOOH, and possibly have developed some covalent character This may partly explain as to why hydroxyl ions in HBO (2) and HBO (3) have not been found exchangeable despite nitrate ions being sorbed

5.1.5 Kinetics of Nitrate Removal by HBO Powders

Among hydrous bismuth oxide powders, yellow colored HBO (2) and HBO (3) showed excellent nitrate sorption (removal) properties at 40 g/L dosage and in 24 h contact time. In order to optimise the contact time in batch operations, kinetics of removal was studied at 1 meq/L nitrate level for HBO (2) and HBO (3). Fig. 5.4 presents the results of these experiments. It was observed that although the removal seemed continuing even after 4h of observation period, most of the sorption occured within initial 2h. Thereafter sorption proceeded rather slowly. HBO (3) showed a slightly faster removal than HBO (2).

For studying the rates of reaction, Helffrich's (1962) first order reversible kinetic model is most frequently used. The sorption of nitrate from liquid phase to the solid phase (of HBOs) may be considered as a reversible reaction with an equilibrium being established between two phases. This can be expressed as
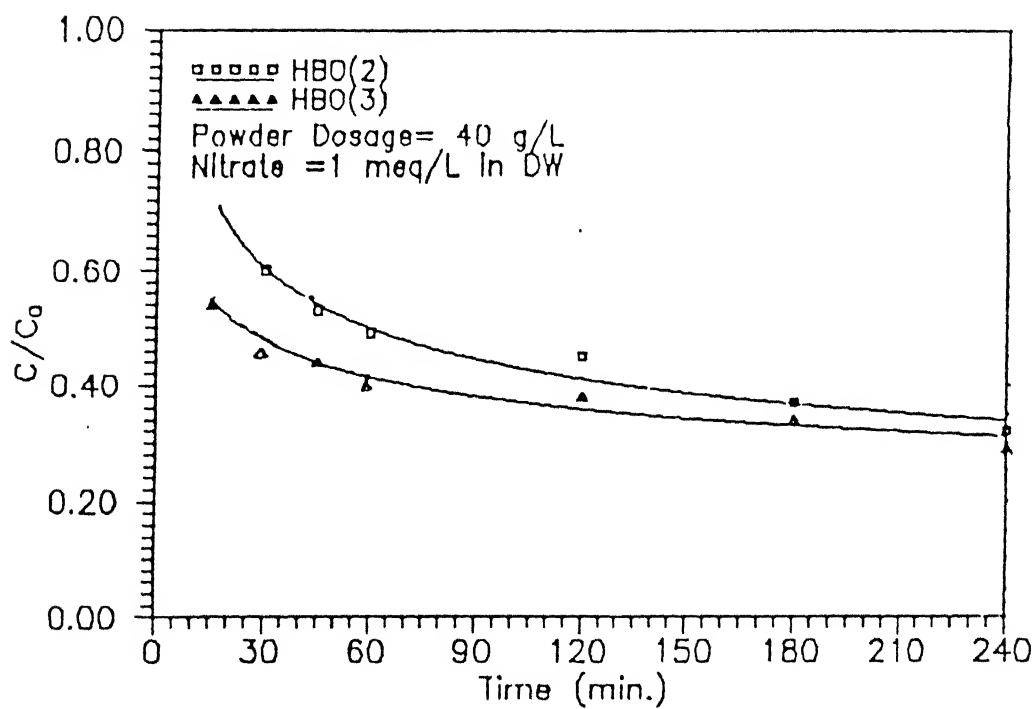
$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \qquad (5.3)$$

Fig. 5.4 Kinetics of Nitrate Removal by HBO Powders.

where A and B are the liquid and solid phases involved in the sorption process, and k_1 and k_2 are first order rate contants. If the first order reversible kinetic model holds true, the rate equation for the reaction is expressed as

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} \tag{5.4}$$

where C_A and C_B are the concentrations of nitrate in solution and on the sorbent at any time t.

If C_{Ai} and C_{Bi} are the initial concentration of nitrate in solution and on sorbent respectively and X_A represents the fractional sorption of nitrate at any time t, then

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} = C_{Ai}\frac{dX_A}{dt} = k_1 C_A - k_2 C_B$$

$$= k_1\left(C_{Ai} - C_{Ai}X_A\right) - k_2\left(C_{Bi} + C_{Ai}X_A\right) \tag{5.5}$$

If C_{Ae} and C_{Be} represents equilibrium concentrations of nitrate in solution and on the sorbent respectively, and X_{Ae} represents fractional sorption of nitrate from liquid, at equilibrium

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} = 0$$

This leads to

$$X_{Ae} = \frac{k_c - (C_B / C_{Ai})}{k_c + 1}$$

(5.6)

where

$$k_c = \frac{C_{Be}}{C_{Ae}} = \frac{C_{Bi} + C_{Ai} X_{Ae}}{C_{Ai} - C_{Ai} X_{Ae}} = \frac{k_1}{k_2}$$

(5.7)

The rate equation in terms of equilibrium conversion can be obtained from equations (5.5), (5.6) and (5.7), i.e.

$$\frac{dX_A}{dt} = \left(k_1 + k_2\right)\left(X_{Ae} - X_A\right)$$

(5.8)

Integrating equation (5.8) and substituting for k_2 from equation (5.7), following form is obtained

$$-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = k_1\left(1 + \frac{1}{k_c}\right)t$$

(5.9)

Putting $\frac{X_A}{X_{Ae}} = U(t)$ and $k_1\left(1 + \frac{1}{k_c}\right) = k'$ in above equation, this transforms to

$$\ln\left[1 - U(t)\right] = -k't$$

(5.10)

where $k' = k_1\left(1 + \frac{1}{k_c}\right) = k_1 - k_2$ and is called first order overall rate constant.

$$U(t) = \frac{X_t}{X_{te}} = \frac{C_{tt} - C_t}{C_{tt} - C_{te}}$$

and is called the fractional attainment of equilibrium at time t (Helffrich, 1962).

$\ln[1 - U(t)]$ vs time was plotted for HBO (2) and HBO (3), as shown in Fig 5.5 and Fig. 5.6 respectively. If Helffrich's first order reversible kinetic model is valid for nitrate sorption on HBO powders, $\ln[1 - U(t)]$ versus t plot should give a straight line, as per equation (5.10). However, from Fig. 5.5, instead of one straight line, a dichotomy is observed for HBO (2). This indicates a biphasic rate of nitrate sorption on HBO (2). The first segment of the dichotomy, having greater slope, suggests a rapid rate of sorption, followed by a relatively slower rate. Similarly for HBO (3) also, Fig. 5.6 shows a dichotomy, indicating a faster rate in the beginning followed by relatively slower rate.

5.2 CHARACTERISATION OF HBOs

5.2.1 Properties of Wet Preciptates

Fritsche (1993) observed removal of nitrate by yellow bismuth hydroxide precipitate and reported that the mechanism is ion exchange with OH^- as counter ion. He passed 20 mL of nitrate water through a bed of 10 g wet precipitates. Our tests also confirmed that HBO (2) and HBO (3) powders (dry precipitates) which were yellow in color, gave significantly higher nitrate
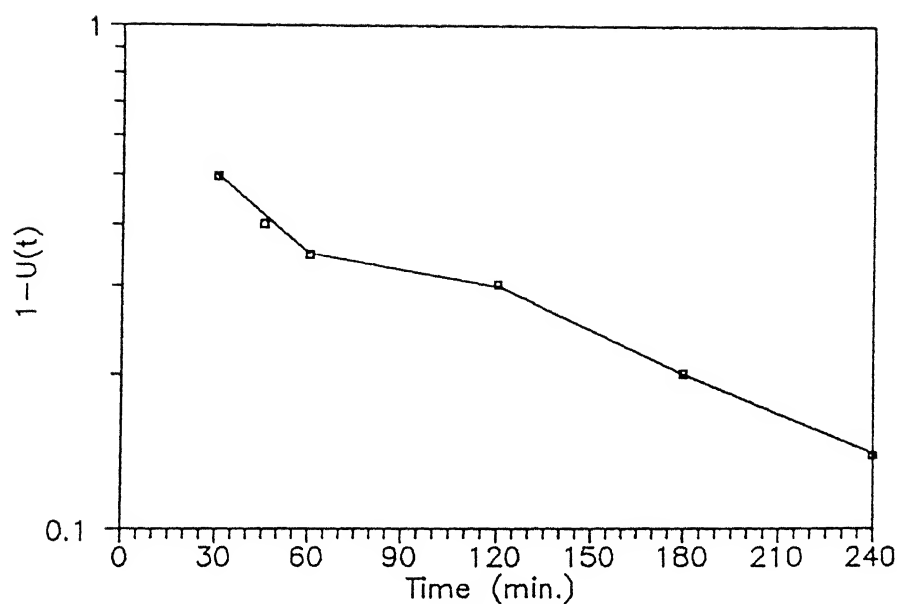
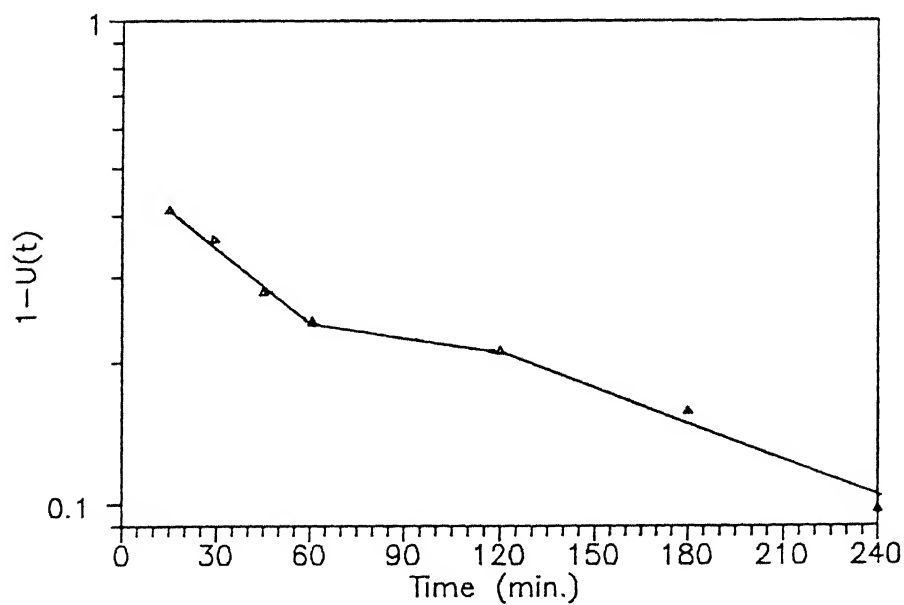Fig. 5.5 First Order Reversible Kinetic Fit for HBO(2)

Fig. 5.6 First Order Reversible Kinetic Fit for HBO(3)

removals than HBO (1) which was white In order to understand the mechanism of nitrate removal by HBOs, the respective precipitates were used in parallel columns and apart from nitrate, pH of effluent was also monitored.

The efflent quality of the three columns are shown in Fig 5.7 (a) and (b) In order to make quantitative evaluation, solid content of the precipitates were estimated. An average of three determinations for each precipitate gave a solid content of 38.38, 15.82, and 17.60% for HBO (1), HBO (2) and HBO (3) respectively. On per unit dry mass basis, each gram of HBO (1), HBO (2) and HBO (3) removed 0.58, 1.20, and 1.40 mg of nitrate respectively at 1 meq/L influent level.

Fig 5.7 (b) shows the variation of pH with effluent volume. The effluent pH from HBO (2) and HBO (3) seemed to be more stable than that from HBO (1) column. Whereas, pH of effluents from HBO (1) varied between 7.0 - 7.8, those from HBO(2) and HBO(3) remained slightly higher but within a narrow range of 7.8 - 8.2.

Fig 5.8 shows the results of an regeneration attempt of beds by 0.1N NaOH Alkalinity expressed in terms of mg $CaCO_3$/L has been applied as a measure of regenerant consumption during the process. It is observed that the regenerant effluents show highest nitrate concentration when the hydroxide consumption by the media is maximum. In quantitative terms, recovery ratio, defined as

Recovery Ratio (RR) = Total nitrate eluted by the regenerant (meq) / Total nitrate sorbed in the bed before regeneration (meq).

(b)

(a)

HBO(1)

Wet Precipitate = 5.0 g
Bed Height=1.50+0.1 cm
Flow=1.20—1.45 mL/min
Dry Weight=1.92 g

HBO(2)

Wet Precipitate=5.0 g
Bed Height=1.50+0.1 cm.
Flow=1.45—2.10 mL/min.
Dry Weight=0.79 g

HBO(3)

Wet Precipitate =5.0 g
Bed Height=2.30+0.1 cm.
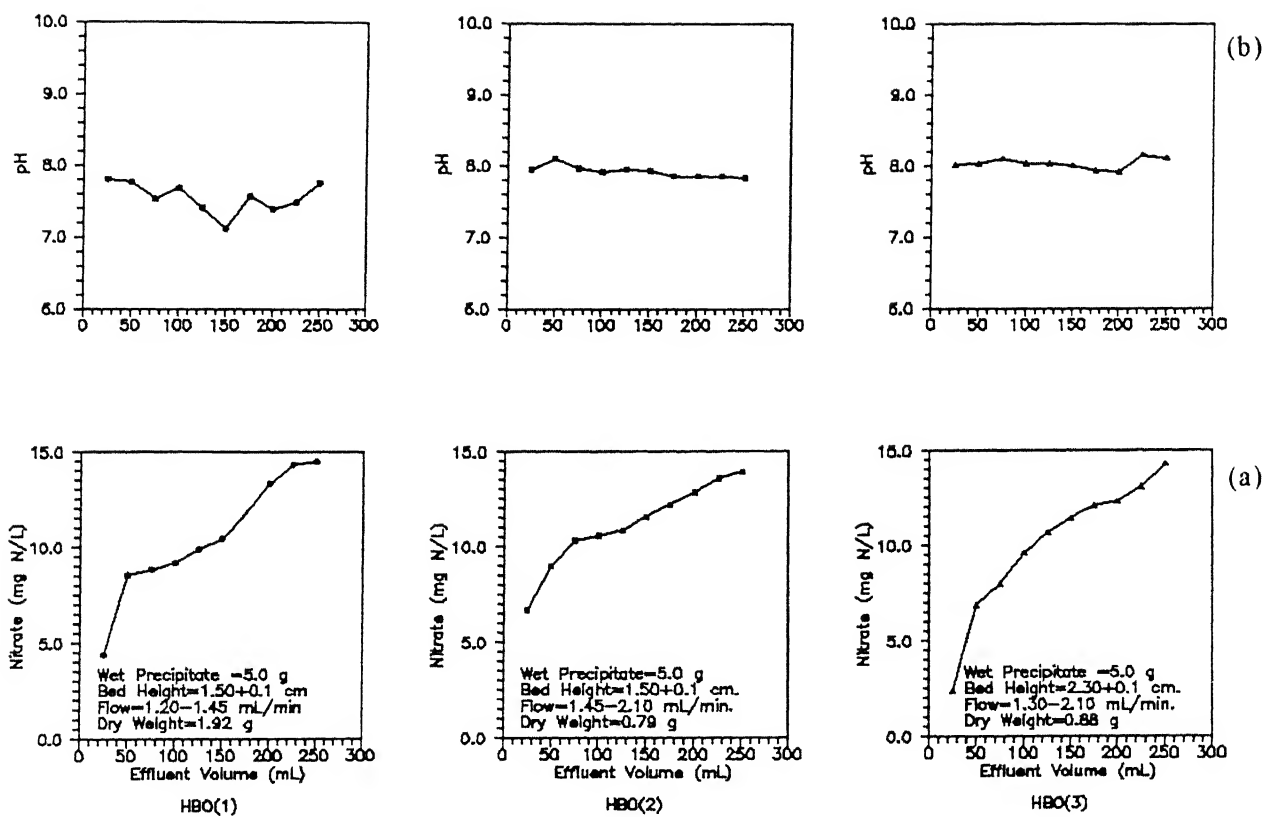Flow=1.30—2.10 mL/min.
Dry Weight=0.88 g

Fig. 5.7 Effluent Quality from HBO Precipitate Columns
with 1 meq/L Nitrate in Distilled Water.
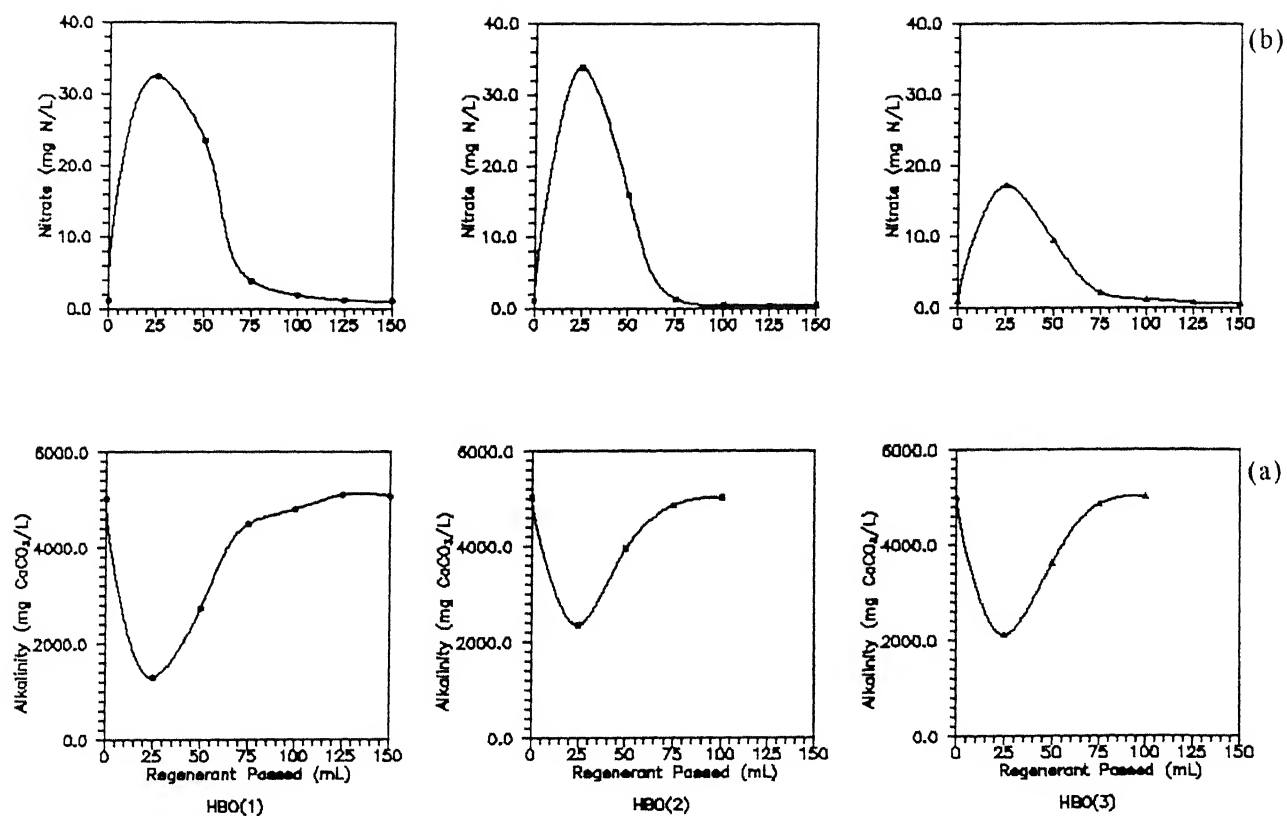
Fig. 5.8 Regenerant Effluent Quality from HBO Precipitate Columns.

is found as 0.95, 0.94 and 0.55 for HBO (1), HBO (2) and HBO (3) respectively

This indicates that HBO (1) and HBO (2) elute most of the sorbed nitrate while

passing 0.1N NaOH, but HBO (3) retains a significant portion of it. Fig 5.9 shows

the effluent qualities through HBO precipitates in first and second cycles

Interestingly, while for HBO (2) and HBO (3) the nitrate uptake properties

decreased. it increased for HBO (1). A deterioration in nitrate uptake properties

of HBO (2) in second cycle even with a recovery ratio of 0.94 in regenerant

effluent indicates that although sodium hydroxide eluted the sorbed nitrate, it did

not regenerate the precipitate. On the contrary, possibly it reduced some active

sites for nitrate. HBO(3) also showed decreased nitrate uptake in the second

cycle For HBO (1) however, there is an effective increase in nitrate uptake

capacity. It appears that while passing 0.1N NaOH. apart from elution of sorbed

nitrate. some transformation occurs in the material. which effectively increases

nitrate uptake by this precipitate. HBO (1), HBO (2) and HBO (3) showed a

nitrate removal of 1.10, 0.68, and 0.98 mg/g respectively in the second cycle.

5.2.2 Specific Gravity of HBO Powders

Specific gravity is an important characteristic of a solid material. An

average of three determinations for each powder gave the mean specific gravity

values of 5.80 ± 0.10, 7.00 ± 0.08 and 6.90 ± 0.10 for HBO (1), HBO (2) and

HBO (3) respectively. Fritsche (1993) noted that gradual addition of NaOH to a

solution prepared by dissolving Bi_2O_3 in HCl yields successive precipitation of

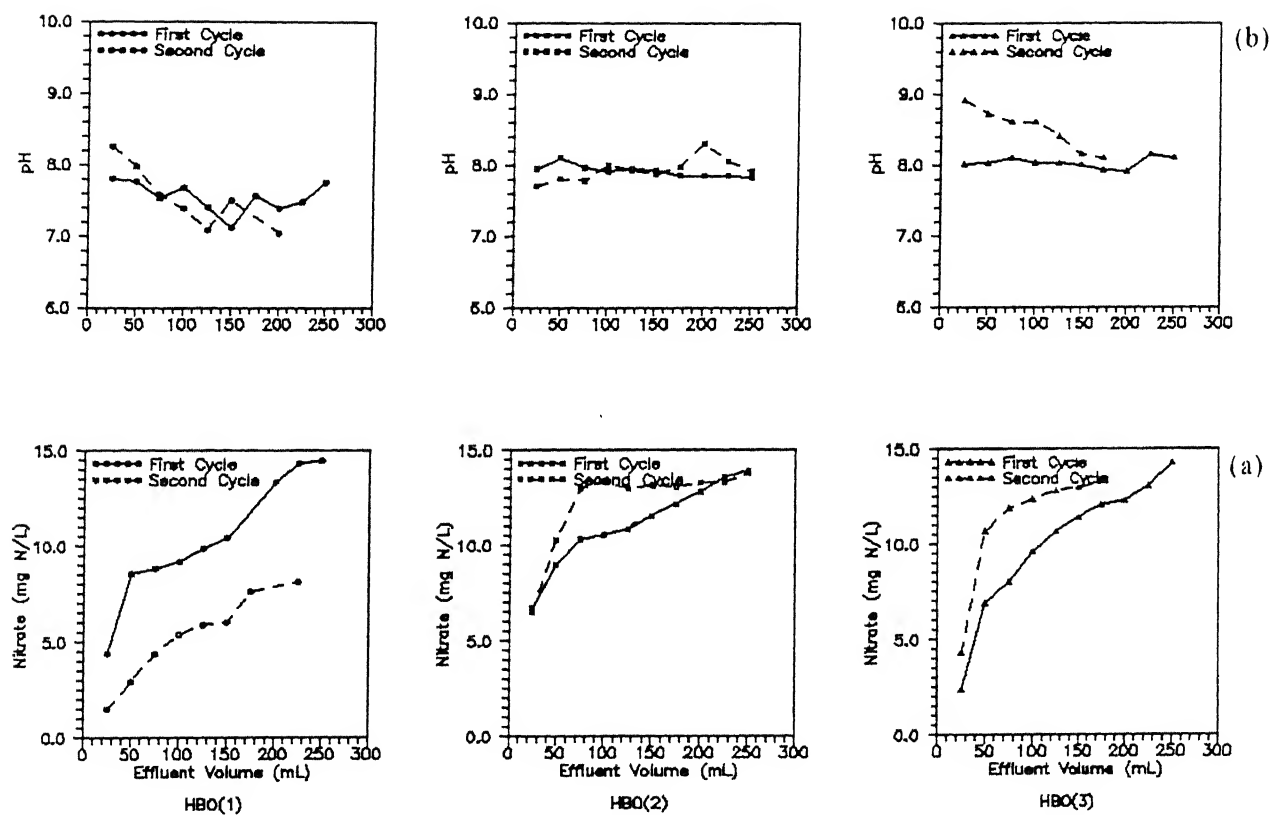white bismuth oxychloride, white bismuth hydroxide and yellow bismuth

Fig. 5.9. Effluent Quality in Two Cycles of Nitrate Loading
on HBO Precipitate Columns.

hydroxide. The color of HBO (1) is almost white Among white compounds, bismuthous hydroxide, $Bi(OH)_3$, has a specific gravity of 4 36, whereas that for bismuth oxychloride is 7.32. The observed specific gravity of 5.80 ± 0.10 for HBO (1) suggests that it is neither pure bismuthous hydroxide. nor bismuth oxychloride. A much closer value to the specific gravity of bismuthous hydroxide, $Bi(OH)_3$, and relatively much lower than that of bismuth oxychloride. suggests that HBO (1) is predominently hydroxide. HBO (2) and HBO (3) are predominently yellow Among yellow compounds. the specific gravity of pure Bi_2O_3 ranges between 8.20 and 8.70. The specific gravity of bismuth oxyhydroxide, which is yellow in color could not be ascertained from the available literature. The specific gravity values of HBO (2) and HBO (3) are fairly close to each other, but much lower than that of pure Bi_2O_3 powder. This suggests that HBO (2) and HBO (3) are different than Bi_2O_3 and possibly the specific gravity of bismuth oxyhydroxide is close to the values observed for HBO (2) and HBO (3).

5.2.3 pH of Point of Zero Charge (pH_{pzc}) of HBO Powders

It was observed that variation of pH did not change the nitrate removal by yellow bismuth hydroxides very appreciably. pH of point of zero charge (pH_{pzc}) is an important characteristic of solid materials which helps to understand their behaviour in aqueous solutions. pH_{pzc} of plain Bi_2O_3, HBO (1), HBO (2) and HBO (3), as determined by the method of Huang of Ostovic (1978) is presented in Table 5.1.

TABLE 5.1

pH$_{pzc}$ of HBO Powders

Powder	pH$_{pzc}$
(1) Plain Bi$_2$O$_3$	8 0 – 8 2
(2) HBO (1)	6.3 – 6.5
(3) HBO (2)	9 7 – 10 1
(4) HBO (3)	9.3 – 9.7

Huang (1977) reported that in absence of specific chemical interactions between the solid sorbent and the electrolyte, the net titration curves usually meet at a point, defined as pH$_{pzc}$. In our experiments, however, the net titration curves for different ionic strengths of the electrolyte met at different levels, thus giving a range rather than a point where pH$_{pzc}$ may lie. A specimen titration curve for HBO (1) is presented in Figure 5.10. A range rather than a clear point of intersection of net titration curves may be due to some interaction between the HBO powders and the sodium chloride electrolyte.

5.2.4 Composition of HBOs

The actual composition of HBOs are not well known. There are numerous indications in the literature that the nature of the anions in a salt solution may have a significant effect on the chemical composition and physical
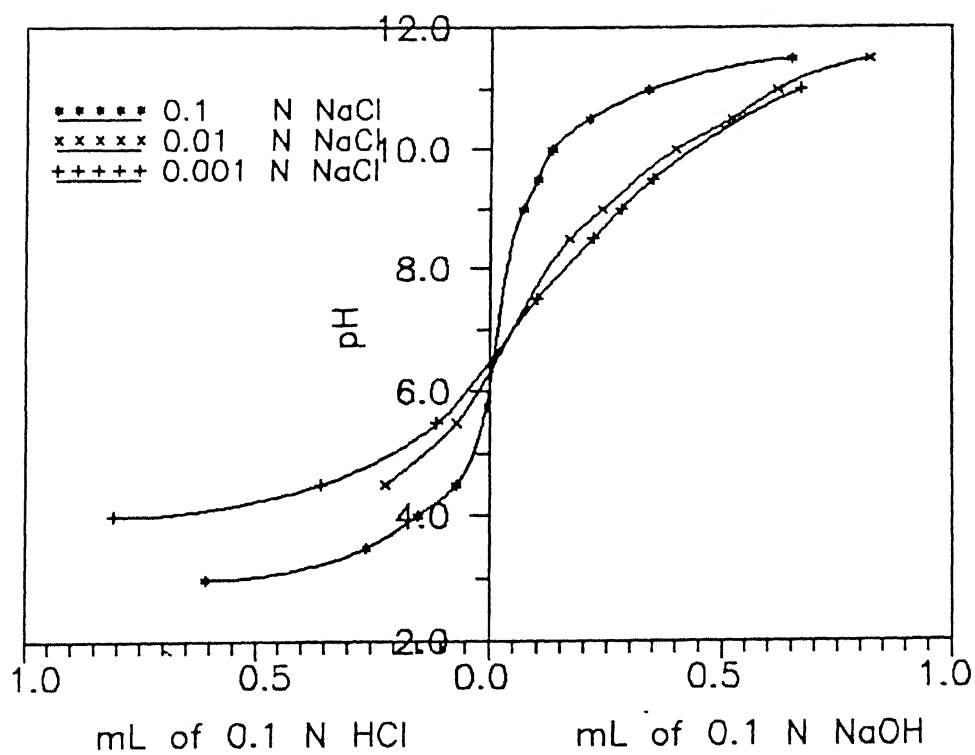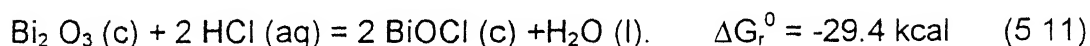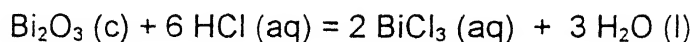
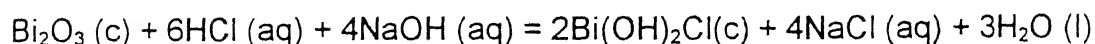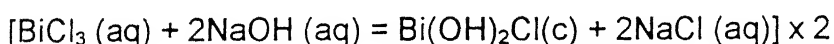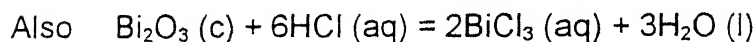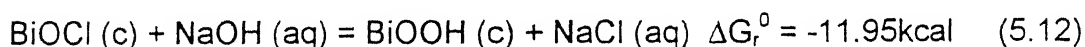Fig. 5.10 pH$_{pzc}$ of HBO(1) Powder

characteristics of the metal hydroxides precipitated from this solution (Scott and Matijevic, 1978). For hydrous ferric oxide precipitate, Biedermann and Chow (1966) noted that rapid precipitation at low base addition (OH/Fe < 0.5) and formation of very stable polymers at high OH/Fe values demonstrate the chloride system to be very much more sensitive to base addition than nitrate or perchlorate systems and the solid phase produced from chloride solutions, β-FeOOH, always contain a variable but significant proportion of chloride. Uniform ferric hydrous oxide sols of varying particle shapes and structures were generated using ferric salts with different anions. The differences apparently arose from varying solute complexes which affected the nucleation and growth stages in the precipitate formation (Matijevic and Scheiner, 1978). For aluminium hydrous oxide sols also, the solids formed in aluminium chloride solutions were found to contain chloride ions, which could be completely leached out by resuspending the particles in a 0.1M HNO_3 solution for 5 days (Scott and Matijevic, 1978). For HBO precipitates, in an analytical attempt, four successive HBOs, designated as HBO (1), HBO (2), HBO (3) and HBO (4) were prepared following the same procedure of mixing 0.1M Bi_2O_3 solution in 2N HCl to 2N NaOH but using successively increasing proportions of as 1:1, 1:2, 1:3 and 1:4 respectively. The mass balance of system of respective precipitates indicated that approximately 280, 110, 40 and 30 mg/g of chloride was retained in HBO (1), HBO (2), HBO (3) and HBO (4) respectively. Remy (1956) while discussing the preparation of $Bi(OH)_3$ noted that it is difficult to obtain in a state of purity as it is colloidal in nature and avidly adsorbs acid anions which are then tenaciously

retained Fritsche (1993) also suspected chloride contamination of yellow bismuth hydroxide precipitate.

BiOCl and $Bi(OH)_2Cl$ are two known solids chloride compounds of bismuth Under preparative conditions, used in the experiments. following reactions may take place:

$$Bi_2O_3 \text{ (c)} + 6 \text{ HCl (aq)} = 2 \text{ BiCl}_3 \text{ (aq)} + 3 H_2O \text{ (l)}$$

$$[BiCl_3 \text{ (aq)} + H_2O \text{ (l)} = BiOCl \text{ (c)} + 2 \text{ HCl (aq)}] \times 2$$

$$Bi_2 O_3 \text{ (c)} + 2 \text{ HCl (aq)} = 2 \text{ BiOCl (c)} + H_2O \text{ (l)}. \qquad \Delta G_r^0 = -29.4 \text{ kcal} \qquad (5\ 11)$$

However, in presence of sodium hydroxide solution. the reaction proceed to

$$BiOCl \text{ (c)} + NaOH \text{ (aq)} = BiOOH \text{ (c)} + NaCl \text{ (aq)} \quad \Delta G_r^0 = -11.95 \text{kcal} \qquad (5.12)$$

Also $\quad Bi_2O_3 \text{ (c)} + 6HCl \text{ (aq)} = 2BiCl_3 \text{ (aq)} + 3H_2O \text{ (l)}$

$$[BiCl_3 \text{ (aq)} + 2NaOH \text{ (aq)} = Bi(OH)_2Cl(c) + 2NaCl \text{ (aq)}] \times 2$$

_____

$$Bi_2O_3 \text{ (c)} + 6HCl \text{ (aq)} + 4NaOH \text{ (aq)} = 2Bi(OH)_2Cl(c) + 4NaCl \text{ (aq)} + 3H_2O \text{ (l)}$$

$$\Delta G_r^0 = -90.89 \text{ kcal} \qquad (5.13)$$

Equation 5.13 indicates that $Bi(OH)_2Cl$ (c) may be formed, when $(OH^-)/(Cl^-) < 1.0$. In presence of sufficient hydroxide,

$$Bi(OH)_2Cl \text{ (c)} + NaOH \text{ (aq)} = Bi(OH)_3 \text{ (c)} + NaCl \text{ (aq)} \quad \Delta G_r^0 = -2.39 \text{ kcal} \qquad (5.14)$$

and $Bi(OH)_3$ (c) $= BiOOH$ (c) $+ 2H_2O$ (l) $\qquad \Delta G_r^0 = -6.53$ kcal   (5.15)
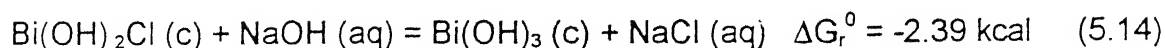
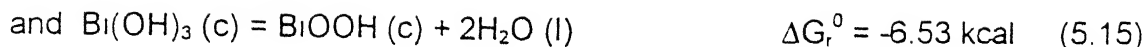Thus, thermodynamic consideration rules out the possibility of these chloride compounds to be the end product of preparation, when $(OH^-)/(Cl^-) > 1\ 0$. However, the feasibility of the reactions for these compounds suggest that they may be a part and the precursors of the final product. Attempts to ascertain the presence of chloride compound in HBO (3) by X-ray diffraction and IR spectroscopic analysis could not be successful. Also only slight qualitative differentiation could be made between X-ray patterns of original and nitrate sorbed HBO (3). Fig. 5.11 shows the X-ray diffraction pattern (30mA/40KV current Cu Kα target) of original and nitrate sorbed HBO (3) powder. Clark (1955) reported that hydrous oxide sols produce X-ray patterns of water and simple oxide or oxide hydrate as for the gels but basic salts containing chloride have no real existence, for in those sols the chloride is merely adsorbed in amounts depending on the size and physical character of the primary particles For hydrous ferric oxide precipitate also. Biedermann and Chow (1966) reported that the solid phase produced had the chemical composition $Fe(OH)_{2\ 70}Cl_{0\ 30}$ and the X-ray pattern of the precipitates was found to agree with that ascribed by previous investigators to "β-FeOOH". This suggests that low molecular weight precursors may be chlorocomplexes, which (a) determine the crystal geometry in addition to the crystal lattice, and (b) do not lose all coordinated halides on being incorporated into the crystal lattice. For hydrous aluminium oxide sols
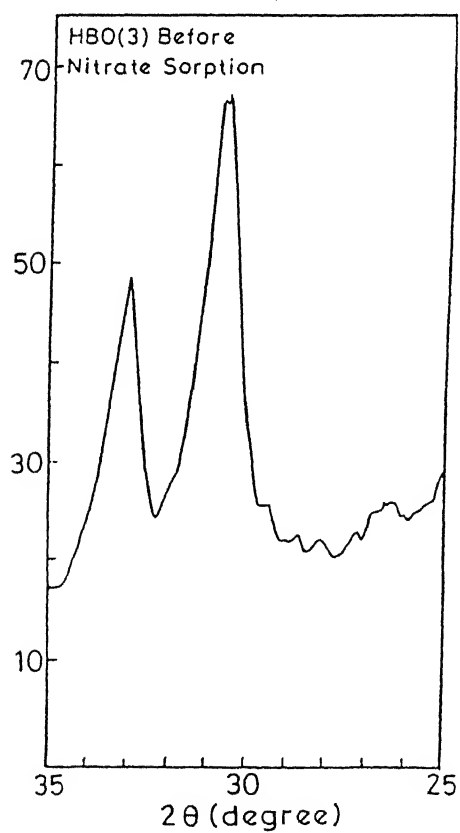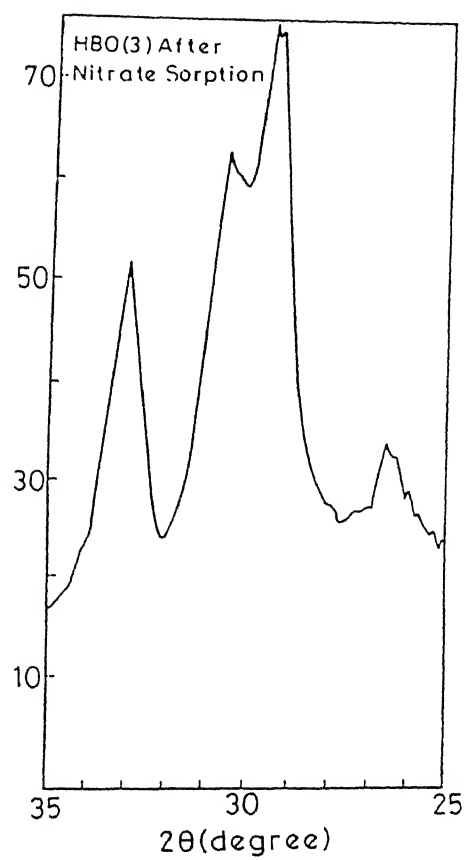
Fig. 5.11 X-Ray Diffraction Pattern of HBO(3) Before and After Nitrate Sorption. (30 mA/40 KV Current, Cu-K_α Target)

also. Scott and Matijevic. (1978) reported that the removal of the chloride ions did not improve the resolution of the X-ray diffraction lines of these systems and no difference in characteristic frequencies (of IR Spectra) could be detected between particles obtained in aluminium chloride and in aluminium perchlorate solutions. In our observation also, the IR did not produce any marked difference in characteristic frequencies of HBO (3) with and without 0.1N NaOH or 0.1N HNO_3 solution treatment. Thus, it appears that chloride ions are retained within these precipitates by rather "weak interaction". Similar observation have been reported by Henry et al.. (1992) for retention of choride ion by aluminium hydroxide pre cipitate formed from chloride solution. Different HBOs had been prepared under the presence of successively increasing volume of hydroxide. When the actual consumption of hydroxide in their preparation were estimated, it was found that approximately 15.1, 25.6 and 26.2% more hydroxide were used in HBO (2), HBO (3) and HBO (4) respectively than HBO (1). These extra consumption of hydroxide changes both the physical as well as chemical properties of the product. It appears that possibly the additional hydroxide are converting more and more residual chloro-compounds to hydroxide and release chloride from the material. The ratio of extra chloride released (meq) to the extra hydroxide consumed (meq), are found to be 0.73, 0.63 and 0.64 for HBO (2), HBO (3) and HBO (4) respectively with respect to HBO (1). A ratio less than 1 possibly indicates that apart from interacting with chlorocompound, the hydroxide is being used in structural reorientation or polymerization of material also.

5.3 SORPTION EQUILIBRIA

Equilibria and kinetics are two important physicochemical aspects of any sorption process. Sorption equilibria intends to determine the ultimate capacity of a sorbent. In any given system, sorption of a solute or ion proceeds until the concentration of solute remaining in the solution is in dynamic equilibrium with that at the sorbent surface. At this position of equilibrium, there is a defined distribution of solute between the solid and liquid phases. A preferred form of depicting this distribution is to express the amount of solute sorbed per unit weight of sorbent as a function of the concentration of solute remaining in solution under equilibrium at constant temperature. An expression of this type is sorption isotherm. Fig 5.12 shows the results of equilibria study conducted for plain Bi_2O_3, HBO (1), HBO (2) and HBO (3) powders for 24h contact time. Based on the shape of isotherm, whereas the sorption by HBO (2) and HBO (3) appears "favourable", it is "unfavourable" for plain Bi_2O_3 and HBO (1).

5.3.1 Langmuir and Freundlich Isotherms

Langmuir and Freundlich models are the most frequently used quantitative equations to describe experimental adsorption data. Langmuir equation is based on the assumption that points of valency exist on surface of the adsorbent and that each of these sites is capable of adsorbing one molecule of adsorbate, so the adsorbed layer will be one molecule thick. Under such conditions,
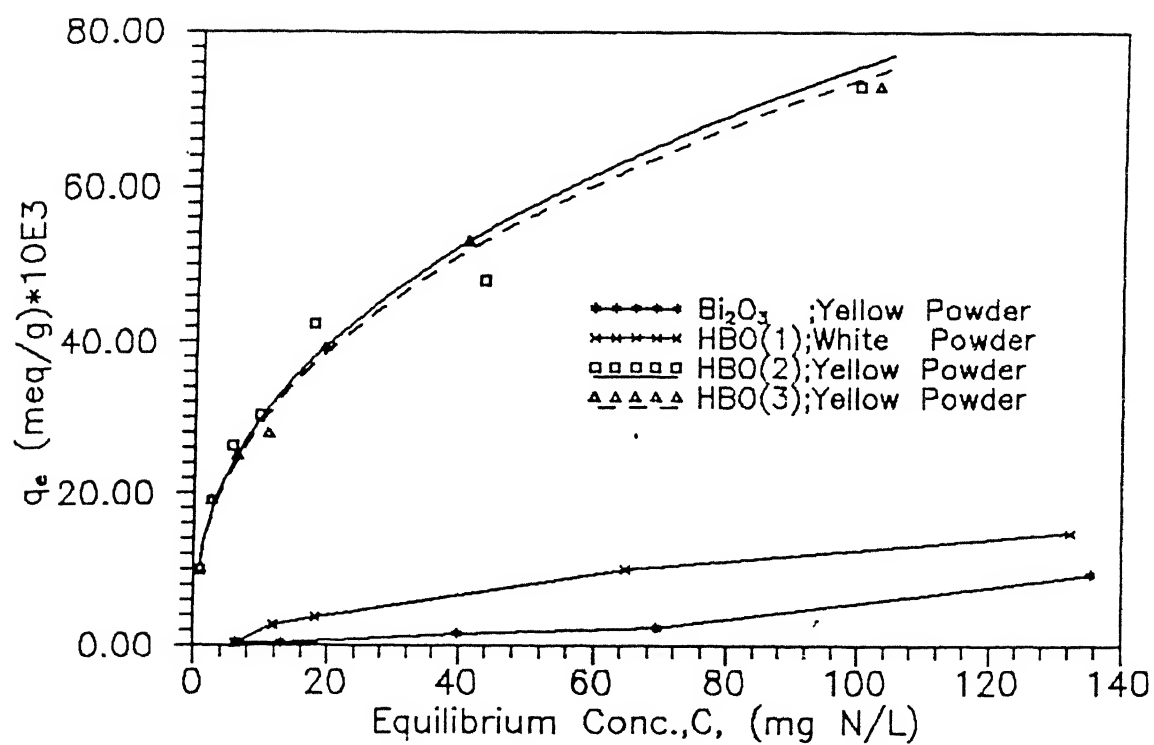
Fig. 5.12 Sorption Isotherm for HBO Powders.

$$q_e = \frac{Q''bc}{1+bc} \qquad (5.16)$$

where q_e = no. of moles of adsorbate per unit weight of adsorbent

Q^o = no. of moles of adsorbate per unit weight of adsorbent to form a complete monolayer on the surface

b = a constant related to energy of adsorption

c = concentration of solute remaining in solution at equilibrium

Rearranging equation (5.16) by putting $k = \dfrac{1}{b}$ gives

$$q_e = \frac{Q^o c}{k+c} \qquad (5.17)$$

Three convenient linear forms of Langmuir equation are

$$q_e = -k\left[\frac{q_e}{c}\right] + Q^o \qquad (5.18)$$

$$\frac{1}{q_e} = \frac{k}{Q^o}\left[\frac{1}{c}\right] + \frac{1}{Q^o} \qquad (5.19)$$

$$\frac{c}{q_e} = \frac{1}{Q^o}(c) + \frac{k}{Q^o} \qquad (5.20)$$

Any of these equations may be used to evaluate k and Q^o from experimental data using graphic or least square analysis (Rubin and Mercer, 1981).

The Freundlich equation has the general form
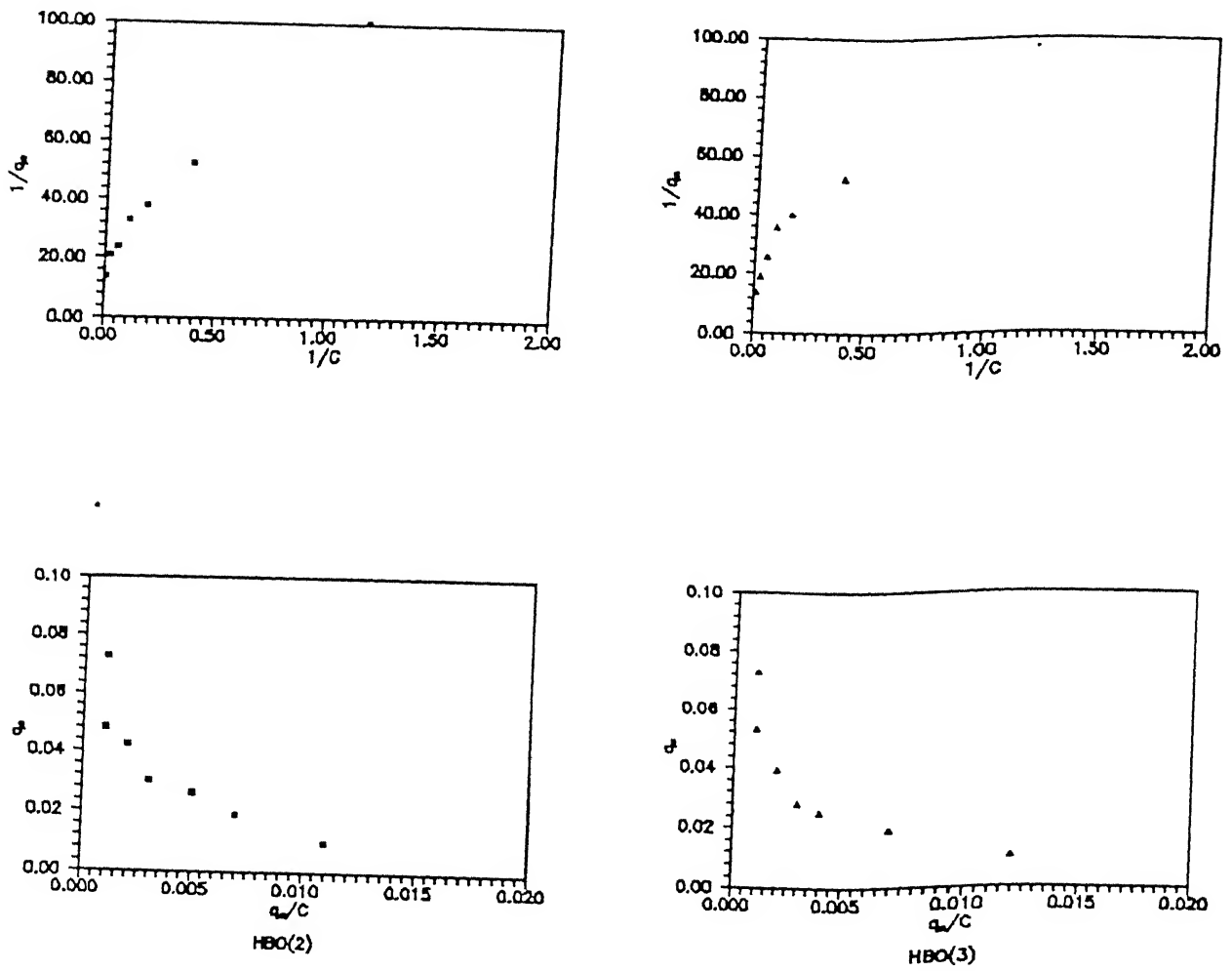
$$q_e = k_F C^{1/n} \qquad (5.21)$$

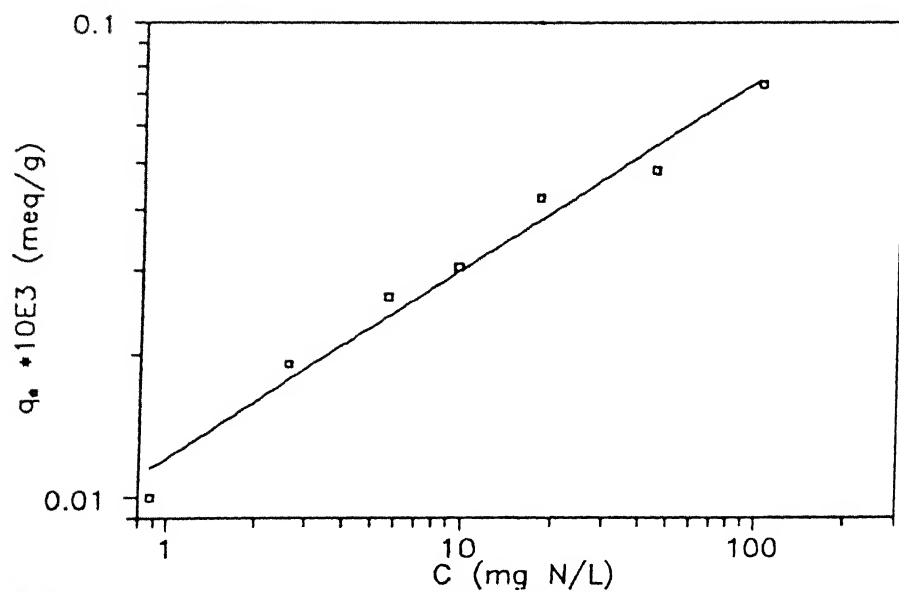Fig. 5.13 Langmuir Isotherm Plot for Nitrate Sorption on HBOs.

Fig. 5.14 Freundlich Isotherm Plot for Nitrate Sorption on HBO(2).
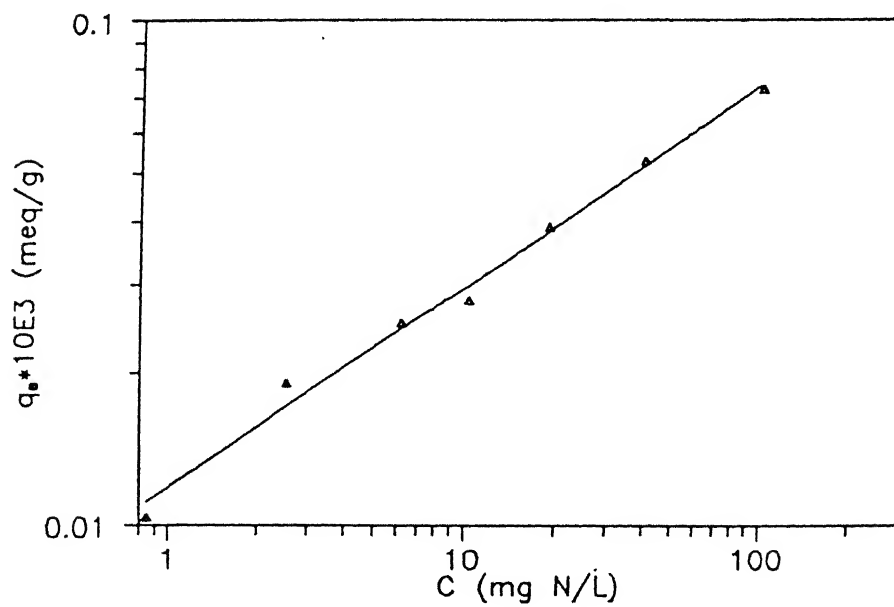

Fig. 5.15 Freundlich Isotherm Plot for Nitrate Sorption on HBO(3).

From these equations. it appears that although the sorption intensity $\left(\frac{1}{n}\right)$ is slightly higher for HBO (3), the sorption capacity (k_F) is greater for HBO (2) than HBO (3).

5.3.2 Chloride Exchange During Equilibria

HBOs have been observed to contain appreciable amount of chloride which can be exchanged with nitrate. During equilibria study, apart from nitrate concentration, chloride level of final water was also monitored for HBO (2) and HBO (3). Figures 5.16 and 5.17 show the results of an analysis of total nitrate sorbed and chloride increased in water for HBO (2) and HBO (3) respectively at different initial nitrate concentrations. There appears a correlation between nitrate taken up by the powder and chloride released by it for both the powders. As the initial nitrate concentration increased, the sorption per unit mass of the sorbent increased, and the release of chloride per unit mass also increased. The Chloride Exchange Ratio (CER), defined as

$$CER = \text{Chloride eluted (meq/g)/Nitrate taken up (meq/g)} \qquad (5\ 25)$$

when plotted against initial nitrate concentrations varies as shown in Fig. 5.18. It is observed that CER of HBO (2) and HBO (3) are in the range 0.75 – 0.85 and 0.65 – 0.79 respectively, and for most of the times. CER for HBO (2) remaines higher than that for HBO (3). This indicates that HBO (2) not only has higher chloride content, its exchange properties are also better than HBO (3).
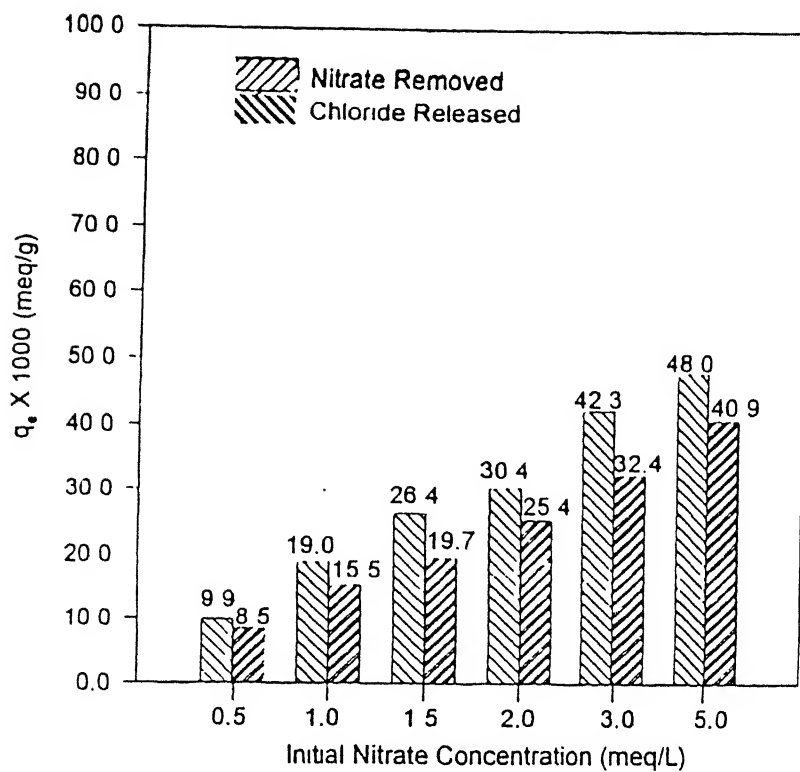
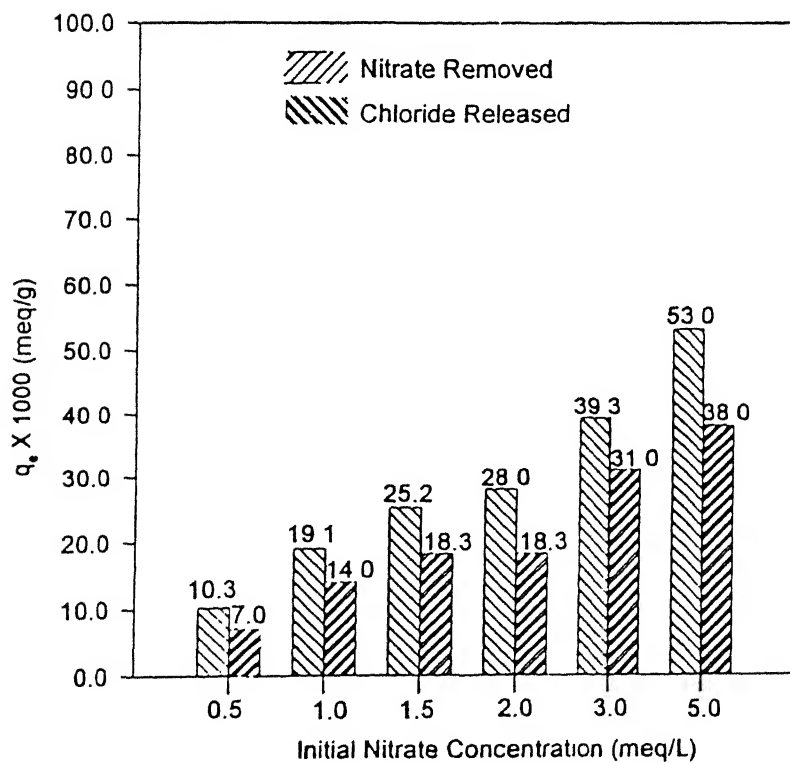Fig. 5.16 Chloride Release from HBO(2)
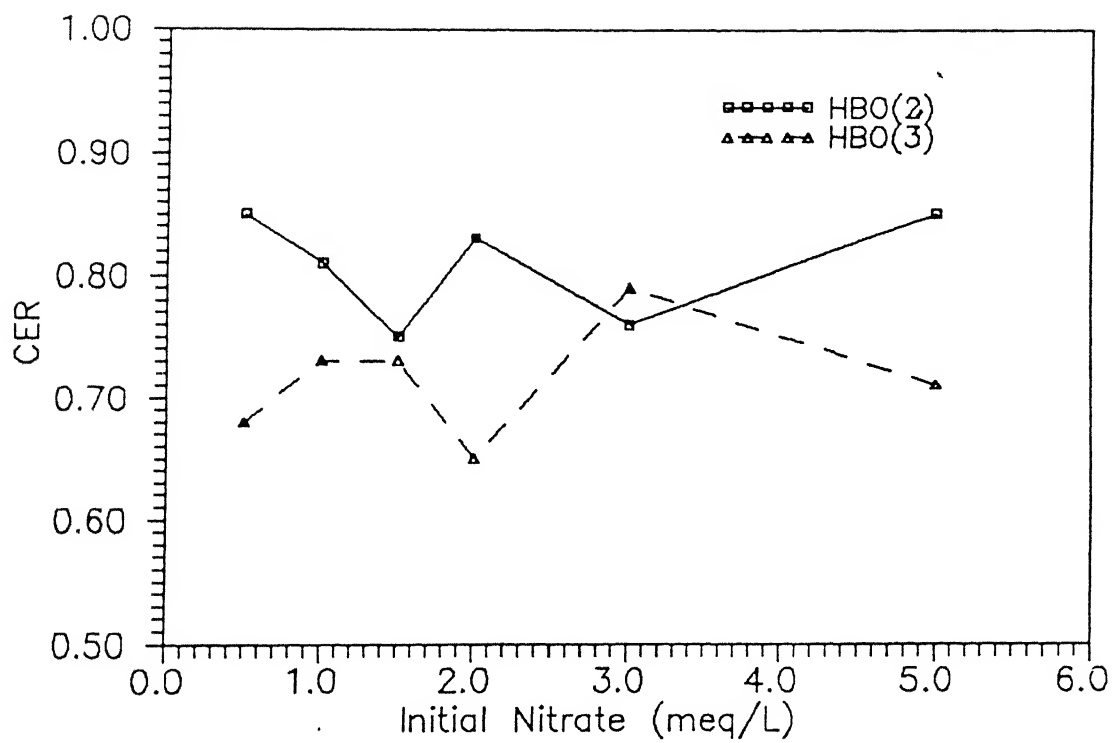

Fig. 5.17 Çhloride Release from HBO (3)

Fig. 5.18 Chloride Exchange Ratio for HBOs.

5.4. PERFORMANCES OF BISMUTH OXYCHLORIDE IN NITRATE

REMOVAL

Observations indicated that chloride was the counter ion for exchange of nitrate by HBO (2) and HBO (3). If chloride compounds or chlorocomplexes were responsible for nitrate removal, bismuth oxychloride. BiOCl should give a better ion exchanger, as bismuthyl ion. BiO^+, mostly forms ionic compounds (Sidwick, 1950). In order to check this possibility, two parallel coloumns, one with 10g of bismuth oxychloride, BiOCl, powder and other with equal amount of HBO (2) were run at an influent nitrate level of 1 meq/L. Effluents were analysed for residual nitrate, pH and chloride concentration. The performance of the col umns are shown in Fig. 5.19. It is observed that while the breakthrough for nitrate from oxychloride powder occured very quickly, HBO (2) continued nitrate sorption for long. The pH of effluent from oxychloride showed frequent lower values towards acidic range. The chloride concentration is increased in the effluent from both the powders, but from oxychloride, it reduces to a low level very sharply. Thus, it appears that in the present form of bismuthyl oxychloride, chloride ions are not suitable free for exchange with nitrate. On the other hand, HBO (2) appears to contain chloride in a much more suitable form (retained by "weak interaction") which apparently exchange with nitrate during column operation.
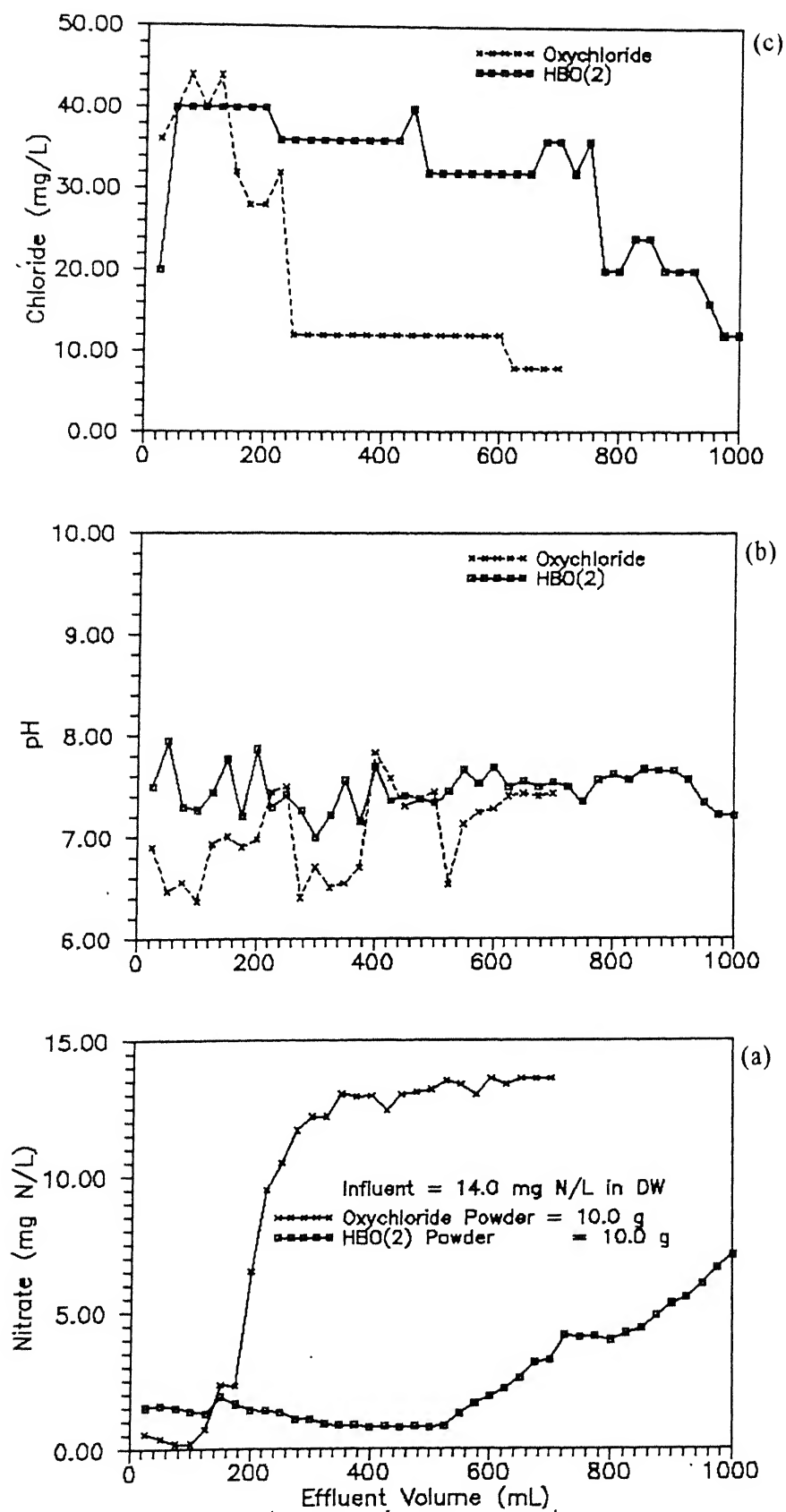
Fig. 5.19 Effluent Quality from Bi-oxychloride and HBO(2) in Columns.

5.5 REGENERATION AND REUSE OF HBO POWDERS

5.5.1 First Cycle

As HBO (1) did not show promising results in equilibria, only HBO (2) and HBO (3) were considered for column studies. Two parallel columns, one with HBO (2) and other with HBO (3) powder, were run simultaneously using 1 meq/L nitrate in distilled water as influent. A controlled flow of 1.10-2.00 mL/min provided an empty bed contact time (EBCT) of 3.5-6.8 minutes for HBO (2) and 2.4-4.8 minutes for HBO (3). Effluent quality in terms of residual nitrate, pH and chloride concentration is shown in Fig. 5.20 (a), (b) and (c) for HBO (2). On segmented basis, Table summarises the nitrate removal and chloride exchange for column with HBO (2) powder.

TABLE 5.2

Performance of HBO (2) Powder in Column

Effluent Volume	NitrateRemoved (meq)	Chloride Released (meq)	CER
(a) 0- 600 mL = 600 mL	0.56	0.54	0.96
(b) 600-1300 mL = 700 mL	0.40	0.38	0.96
(c)1300-1750 mL = 450 mL	0.09	0.08	0 96
Total = 1750 mL	1 05	1 00	0.96

Fig. 5.20 Effluent quality for HBO(2) Columns.

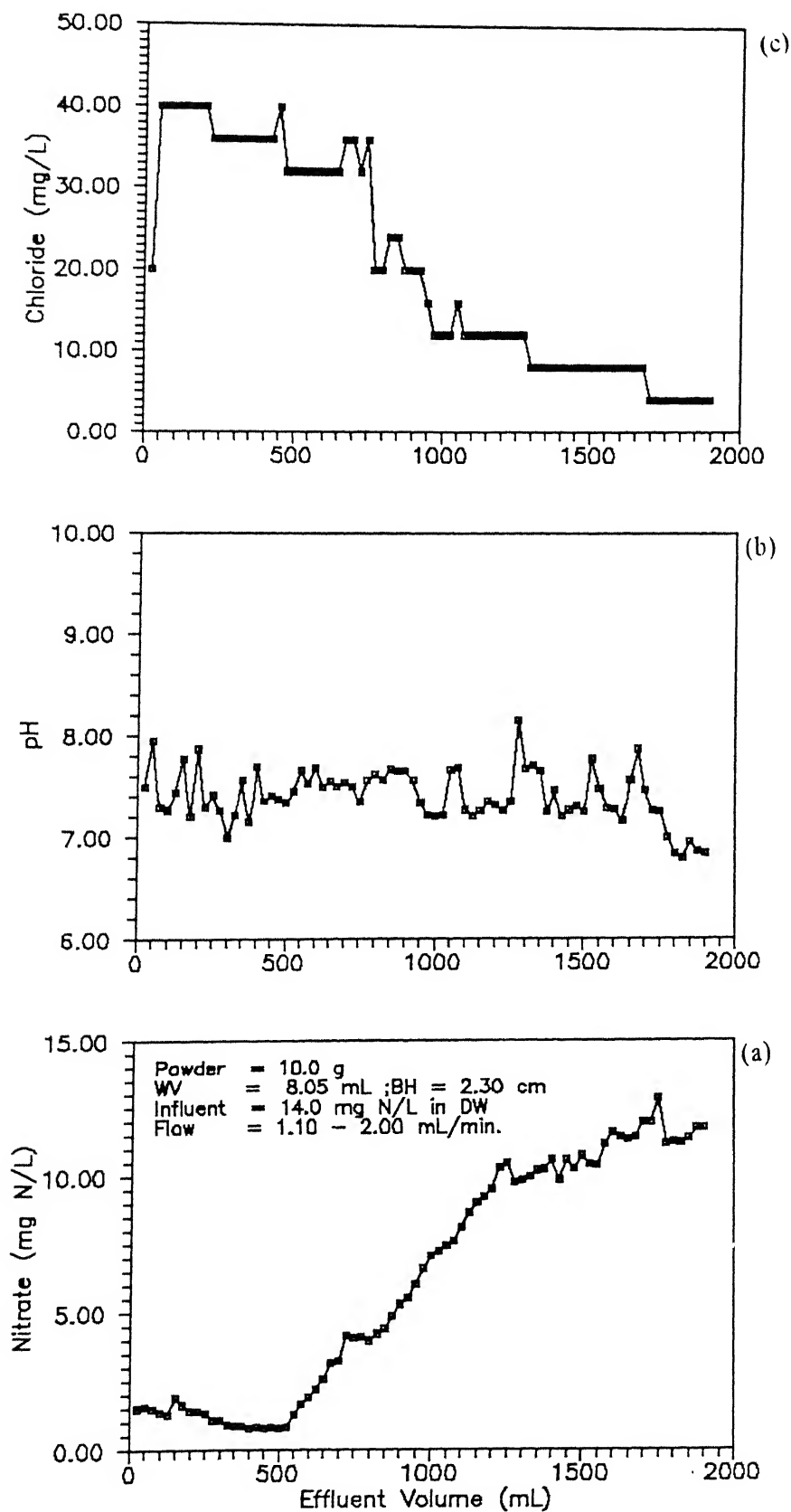The pH value of almost all samples remained within the range of 7.0-8.0. Similarly, Fig. 5.21 (a), (b) and (c) show the effluent quality from HBO (3) powder Table   summarises the performance of this column

TABLE 5.3

Performance of HBO (3) Powder in Column

Effluent Volume	Nitrate Removed (meq)	Chloride Released (meq)	CER
(a) 0-400 mL = 400 mL	0.357	0.315	0.88
(b) 400-750 mL = 350 mL	0.250	0.200	0.80
(c) 750-950 mL = 200 mL	0.090	0.070	0.77
(d)950-1350 mL = 400 mL	0.100	0.090	0.90
(e)1350-1800 mL=550 mL	0.100	0.092	0.92
Total = 1900 mL	0.897	0.767	0.85

Considering the mass of powder in the column (10 g in each), the nitrate removal capacity by HBO (2) and HBO (3) powders are found as 1.4 and 1.3 mg/g at 1 meq/L influent concentration.

5.5.2 Regeneration by Sodium Chloride Solution

In wet precipitate experiments, it was observed that for HBO (2) and HBO (3), although the sorbed nitrate was eluted by passing 0.1N NaOH, the media could not be regenerated. Also, it has been observed that chloride is the exchange ion for nitrate uptake by the media. Hence, it was thought appropriate to regenerate the media by passing 0.1N NaCl in downflow mode. Measurement
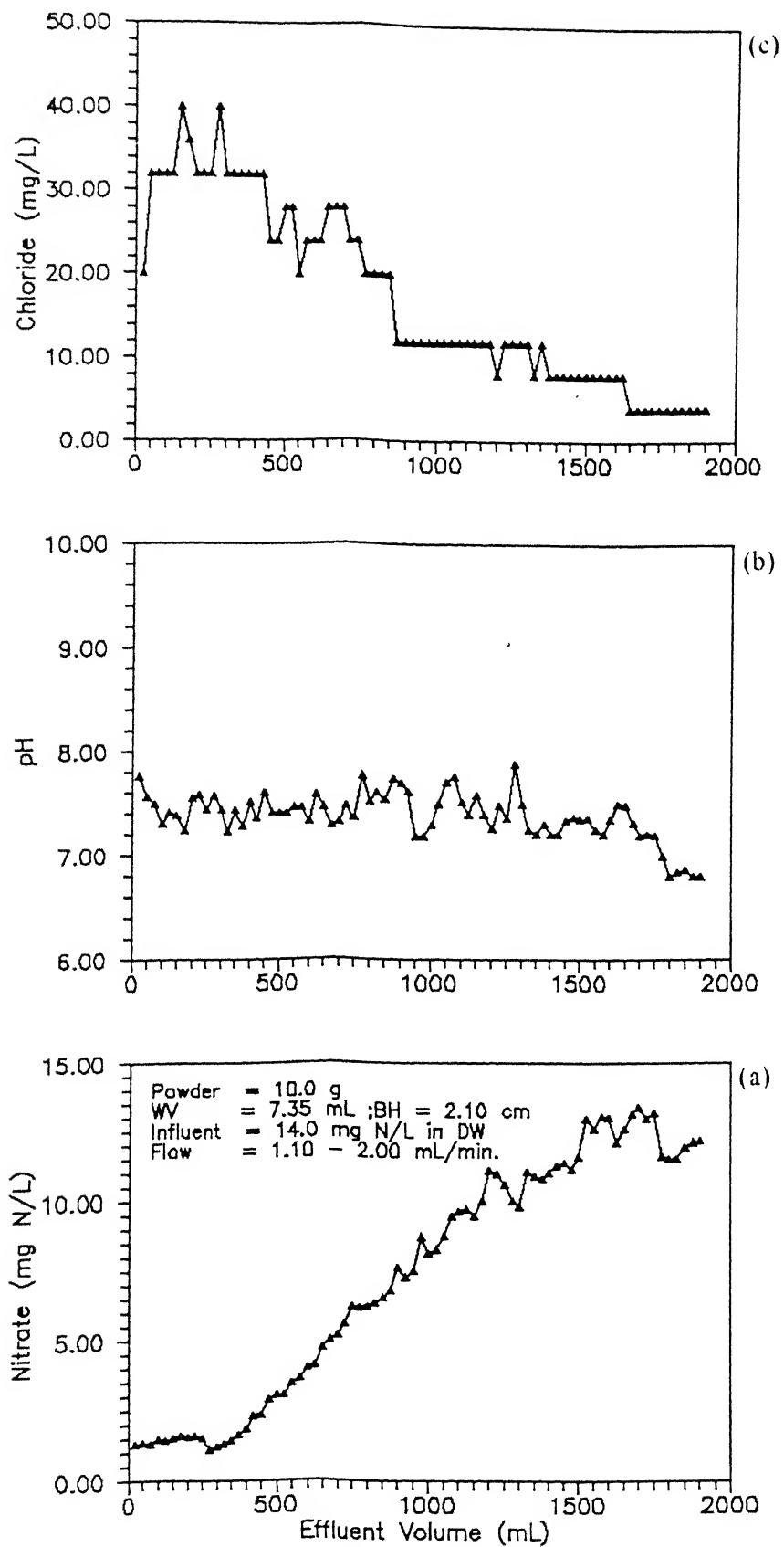
Fig. 5.21 Effluent Quality for HBO(3) Columns.

of nitrate ın regenerant effluent ıs shown in Fıgure 5 22 On mass basıs. the recovery ratıo. ı.e ,the ratio of total nıtrate eluted during regeneratıon to the total nıtrate taken up during sorption for HBO (2) and HBO (3) are found to be 0 60 and 0.49 respectively.Thıs shows that although the recovery ratio for both the powders are low. HBO (2) powder gives better recovery than HBO (3) Wıth respect to the precıpıtate experıments, two significant changes have occurred ın the case under consideration: firstly, the precipitate has been dehydrated and secondly. the regenerant has been changed from 0.1N NaOH to 0.1N NaCl Both of these changes may affect the recovery of sorbed nitrate from the bed. Whereas the dehydration of gel may reduce the rate of mass transfer of ıons from the bed, the nature of chemical used as regenerant may influence the mechanism of the process. The elution of sorbed nitrate by chloride durıng regeneration may be due to higher preference and concentration gradient effect Sodium hydroxide has the advantage of affecting the pH of the envıronment, thereby affecting the dissociation of sorbed ion. Thıs may partly explaın hıgher recovery ratio of nitrate using 0.1N NaOH than 0.1N NaCl.

5.5.3 Second Cycle

After regeneration and distilled water washing, the second cycle was started by passing 1 meq/L nitrate solution through the columns. The performance of the two columns for nitrate removal in first and second cycle are shown in Fig. 5.23 and 5.24 for HBO (2) and HBO (3) respectively. The figures clearly show that columns have been regenerated after passing 0.1N NaCl
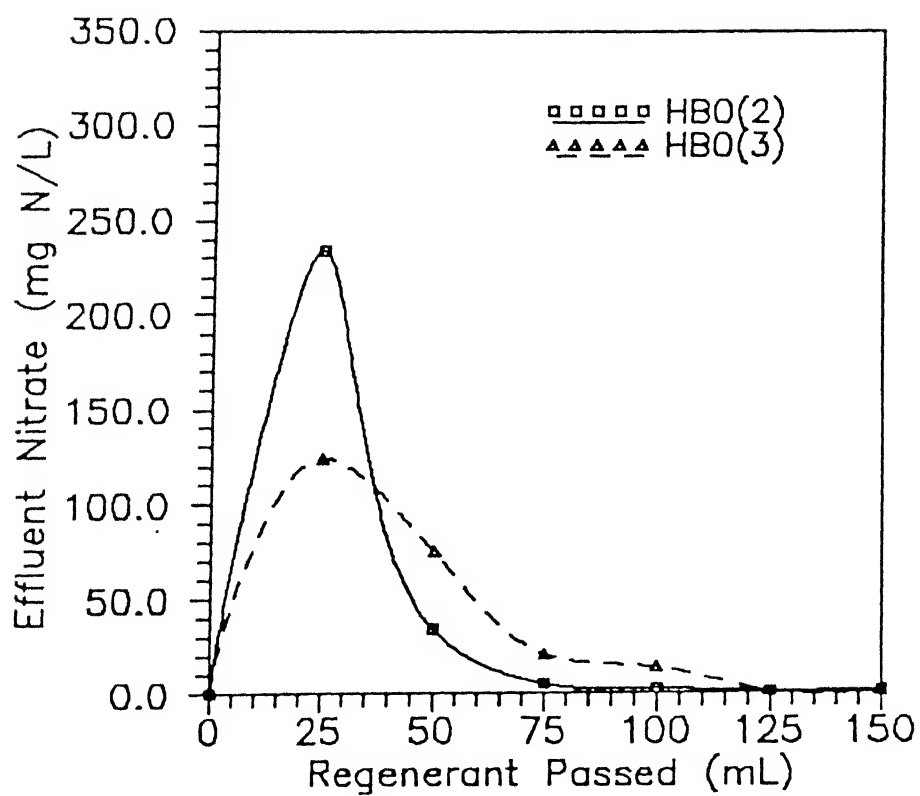
Fig. 5.22 Regeneration of Columns.
(Regenerant: 0.1N NaCl).

solution As chloride ion appears to be the ion of exchange with nitrate so its replenishment is essential for reuse of the media. While sodium hydroxide solution may elute the sorbed nitrate from media. it does not replenish the chloride ions into the media. Sodium chloride solution replenishes the chloride in the matrix of the media making them capable of further nitrate exchange. A rough estimate of mass of nitrate taken up and chloride exchanged from both the powders in second cycle are summaries in Table 5.4

Presence of nitrate in second cycle occured relatively earlier than the first run for both the powders. A comparative observation of Fig. 5.23 and 5.24 reveals that the effluent nitrate concentration from HBO (2) column is consistently lower than that from HBO (3). In first cycle of nitrate application also the relative trend was similar to this only. These observations point towards a slightly better performance of HBO (2) than HBO (3) in column operations.

TABLE 5.4

Summary of Performance of Powders in Second Cycle

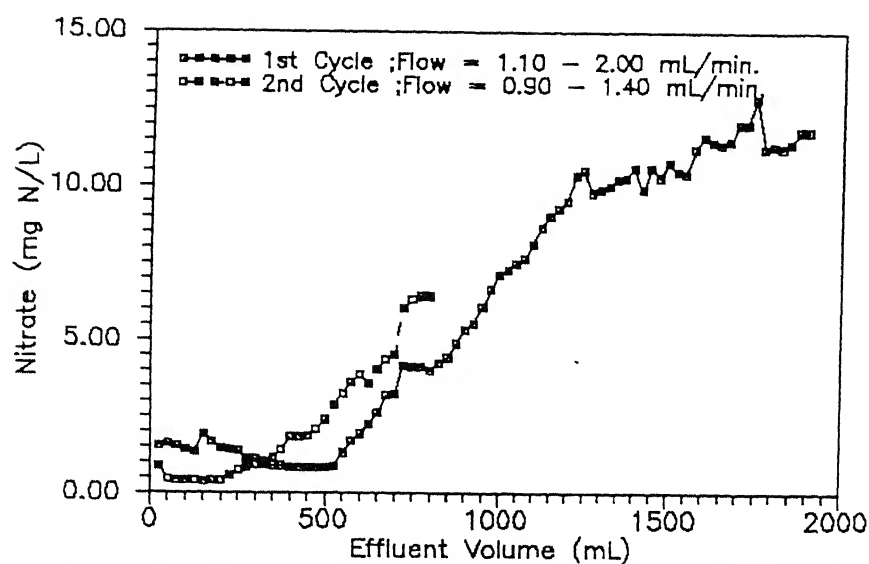| Effluent Volume	Nitrate Removed (meq)	Chloride Released (meq)	CER
HBO (2)			
0 – 500 mL = 500 mL	0.50	0.42	0.84
500 – 800 mL = 300 mL	0.21	0.17	0.80
HBO (3)			
0 – 400 mL = 400 mL	0.31	0.25	0.80
400 – 850 mL = 450 mL	0.28	0.23	0.82

Fig. 5.23 Effluent Nitrate Concentration from HBO(2) Column in First and Second Cycles.
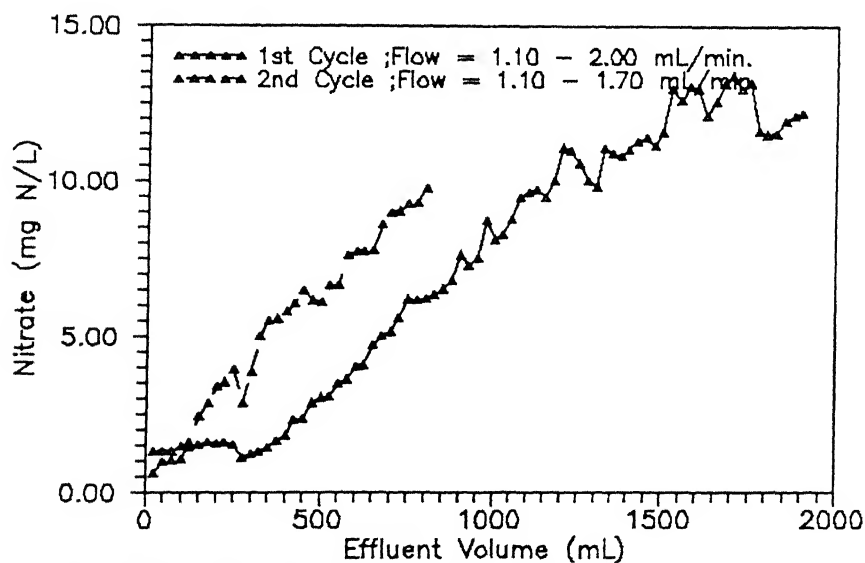

Fig. 5.24 Effluent Nitrate Concentration from HBO(3) Column in First and Second Cycles.

5.5.4 Second Regeneration and Third Cycle of Nitrate Removal

After the second cycle. the columns were regenerated again using 0 1N NaCl An analysis of nitrate concentration in regenerant effluent once again confirmed the elution of sorbed nitrate from the media, as shown in Fig 5 25. After distilled water washing of columns to wash free chloride, the columns were run with 1 meq/L nitrate in distilled water as influent for the third cycle. Table 5 5 summarises the observations for nitrate removed and chloride released during the third cycle.

TABLE 5.5

Summary of Performance of Powders in Third Cycle

Effluent Volume	Nitrate Removed (meq)	Chloride Released (meq)	CER
HBO (2)			
0 – 400 mL = 400 mL	0.40	0.34	0.85
400 – 700 mL = 300 mL	0.19	0.16	0.84
700 – 1000 mL= 300 mL	0.09	0.08	0.88
HBO (3)			
0 – 200 mL = 200 mL	0.18	0.16	0.88
200 – 600 mL = 400 mL	0.23	0.20	0.86
600 – 750 mL = 150 mL	0.05	0.04	0.80

Figures 5.26 and 5.27 show effluent nitrate concentrations from HBO (2) and HBO (3) columns respectively in first, seconc and third cycles. Within the limits of observations made, it is important to note that for HBO (2) powder, the
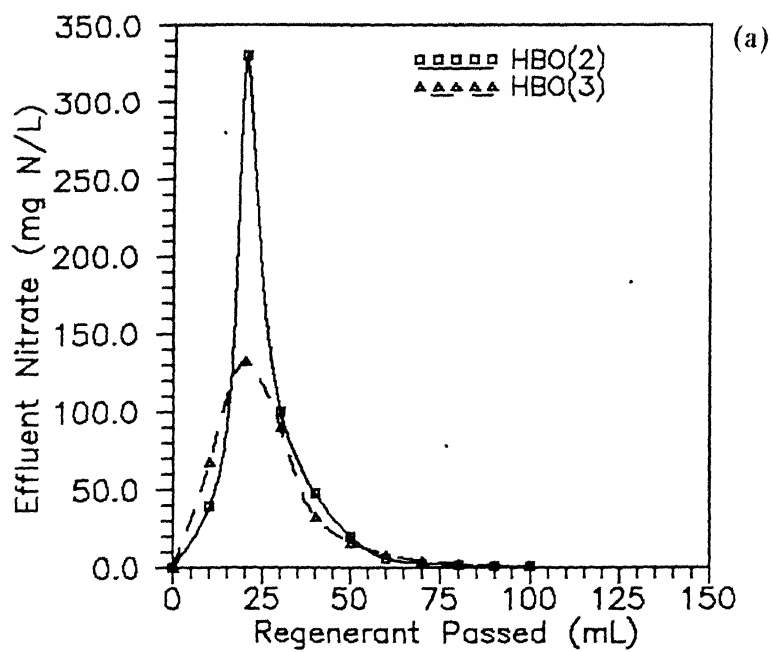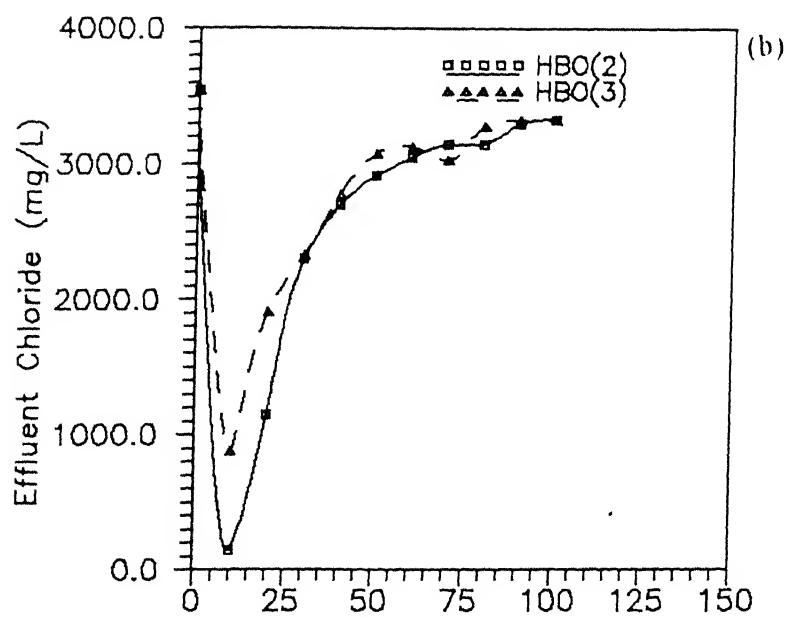
Fig. 5.25 Second Regeneration of Columns
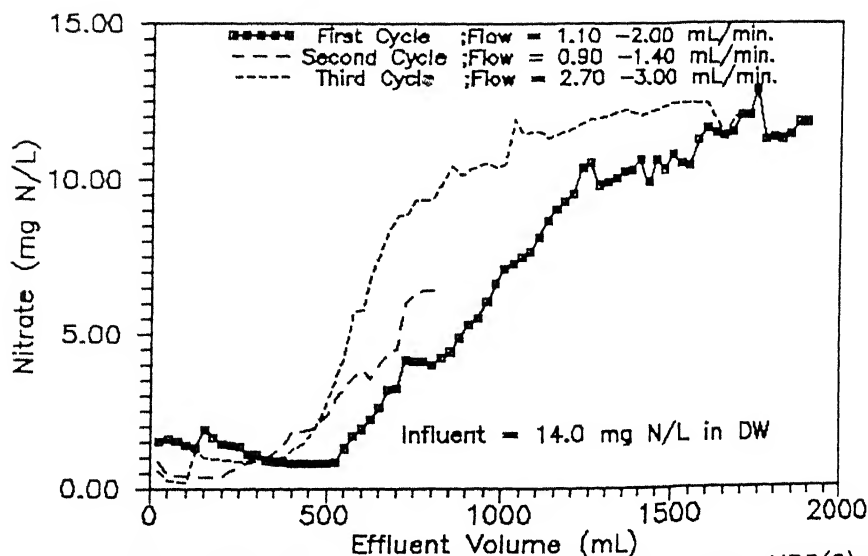(Regenerant: 0.1N NaCl).

Fig. 5.26 :Effluent Nitrate Concentration from HBO(2) Column
in First, Second & Third Cycles.
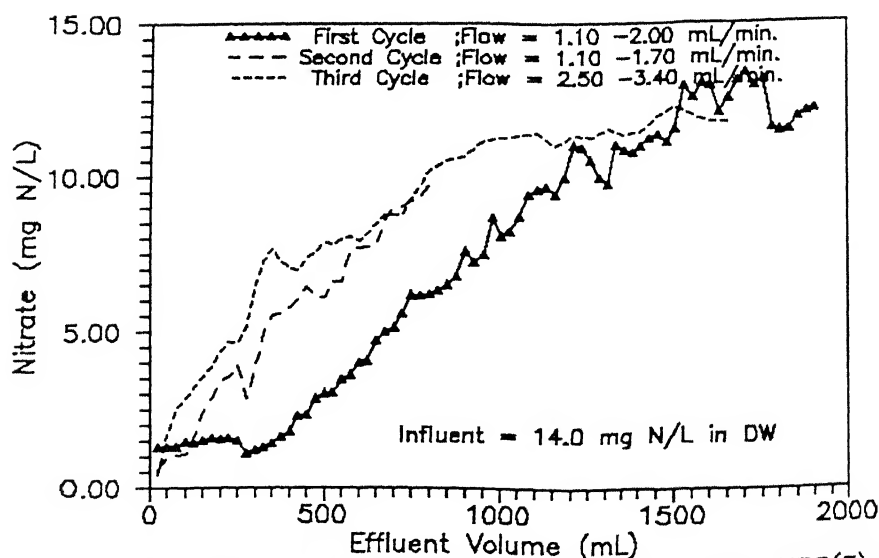
Fig. 5.27 :Effluent Nitrate Concentration from HBO(3) Column
in First, Second & Third Cycles.

effluent nitrate concentration exceeded the permissible limit of 10.0 mg N/L after treating around 1350, 900 and 850 mL in first, second and third cycles respectively. HBO (3) treated approximately 1150, 850 and 800 mL in three respective cycles before exceeding the permissible limits This indicates that although performance of both the powders are closely following, still HBO (2) has slight edge over HBO (3). With only 10 0 g of powder in column, purification of approximately one liter of water in each cycle suggests that HBO powders are highly promising. Also, the regeneration of media with sodium chloride make their use simple and attractive.

Figures 5.28 and 5.29 show the variation of pH through HBO (2) and HBO (3) respectively in first and third cycles. pH of treated water remained within 7 0-8.0. This clearly indicates that OH^- is not working as the exchange anion for nitrate removal by HBO powders.

Figures 5.30 and 5.31 show the variation of chloride through HBO (2) and HBO (3) columns in first and third cycle. These figures indicate that the media get regenerated by O.IN NaCl and exhibit in a similar performance in successive cycles.

5.6 SORPTION OF BICARBONATE AND SULFATE

Apart from nitrate and chloride, bicarbonate and sulfate are other anionic constituents in drinking water. Their sorption behavior on HBO powder were studied using HBO (2) as representative sorbent.

Fig. 5 28 Variation of pH Through HBO(2) Column
in First & Third cycles.
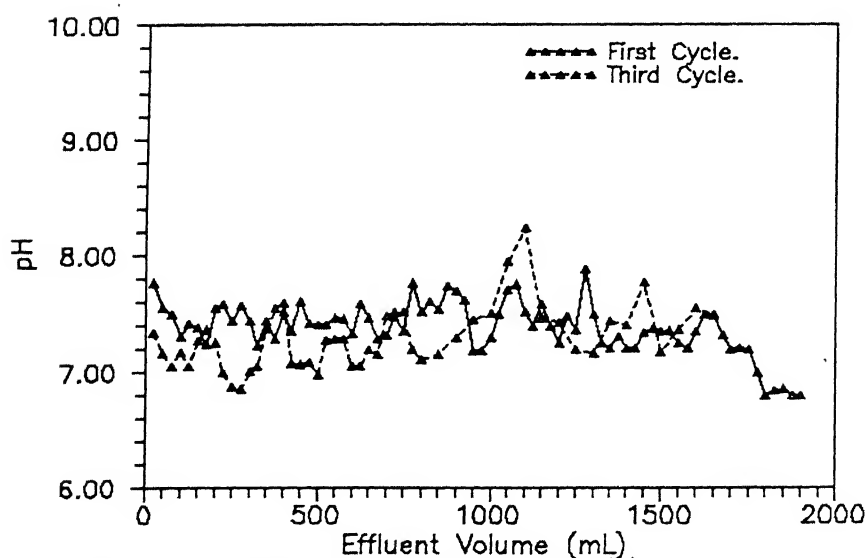
Fig. 5.29 Variation of pH Through HBO(3) Column
in First & Third cycles.
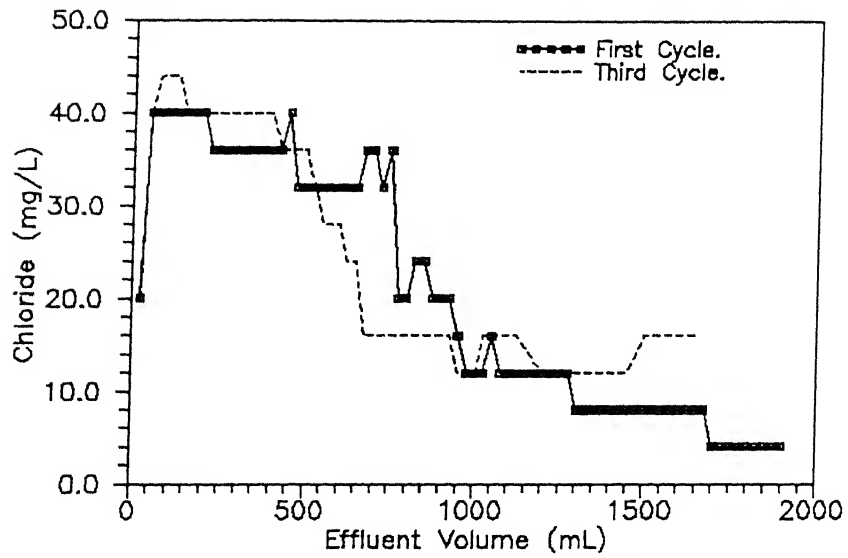
Fig. 5.30 Variation of Chloride through HBO(2) Column
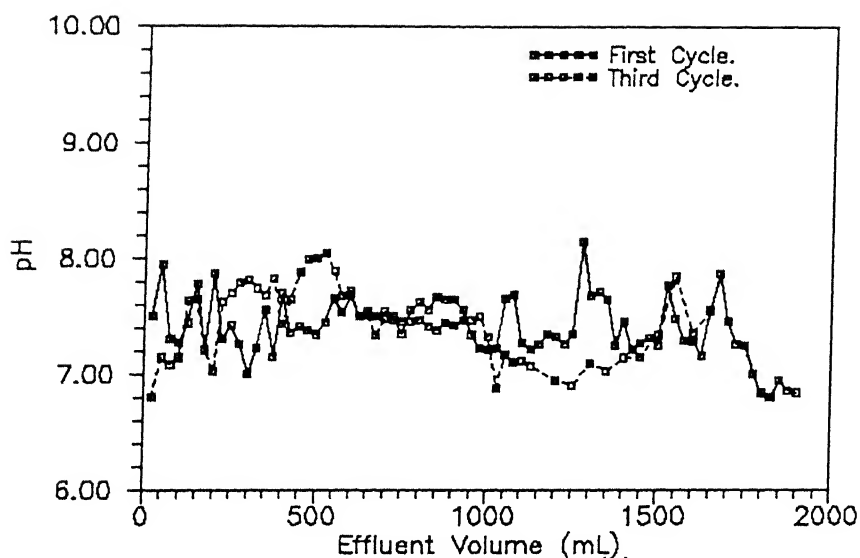
in First and Third Cycles.
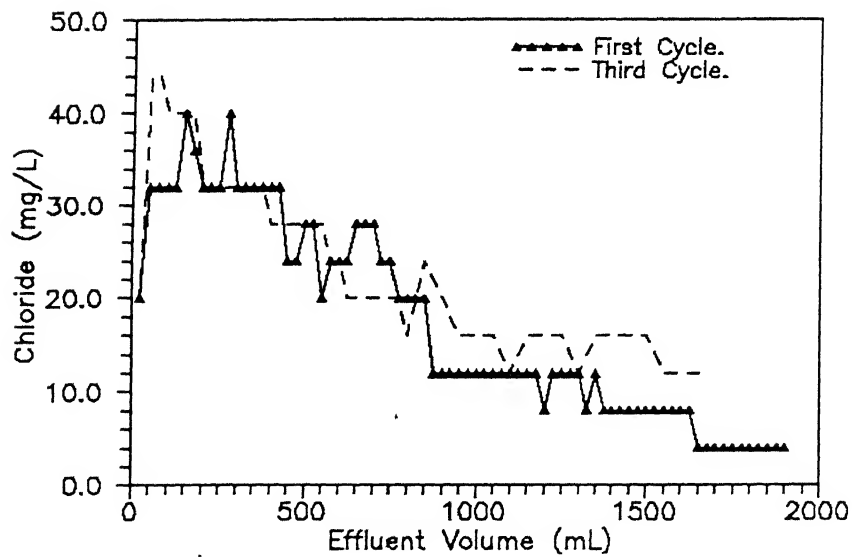
Fig. 5.31 Variation of Chloride through HBO(3) Column

in First and Third Cycles.

5.6.1 Sorption of Bicarbonate

Bicarbonate is normally present in ground and surface waters and gives alkalinity to it. Results of bicarbonate alkalinity sorption on 5.0g HBO (2) powder are shown in Fig. 5.32. It is observed that when influent alkalinity is 1 meq/L, most of it gets sorbed. The pH of effluent ranged between 7.5 to 9.0 The increased chloride concentration in the effluent indicated chloride exchange for bicarbonate sorbed. A rough estimation of chloride exchange ratio (CER) for bicarbonate indicated that CER decreses with the increasing effluent volume. (CER = 0.84 upto 250mL of effluent; 0.74 between 250-750mL). When the influent alkalinity level was raised to 10 meq/l (comparable to ground water bicarbonate level) and the effluent quality was monitored, it was observed that the powder sorbed more bicarbonate alkalinity and also released more chloride. A dynamic equilibrium between the ions present in the influent and the media appears controlling the extent of sorption and breakthrough of bicarbonate.

5.6.2 Sorption of Sulfate

The performance of 5.0g HBO (2) powder in column with approximately 1 meq/L of sulfate solution as influent is shown in Fig. 5.33. It indicates that sulfate is also sorbed over HBO (2) powder , mostly through ion exchange with chloride A CER of around 0.90 is observed for sulfate sorption on HBO (2). The pH of effluent remain mostly between 8.0-9.0.
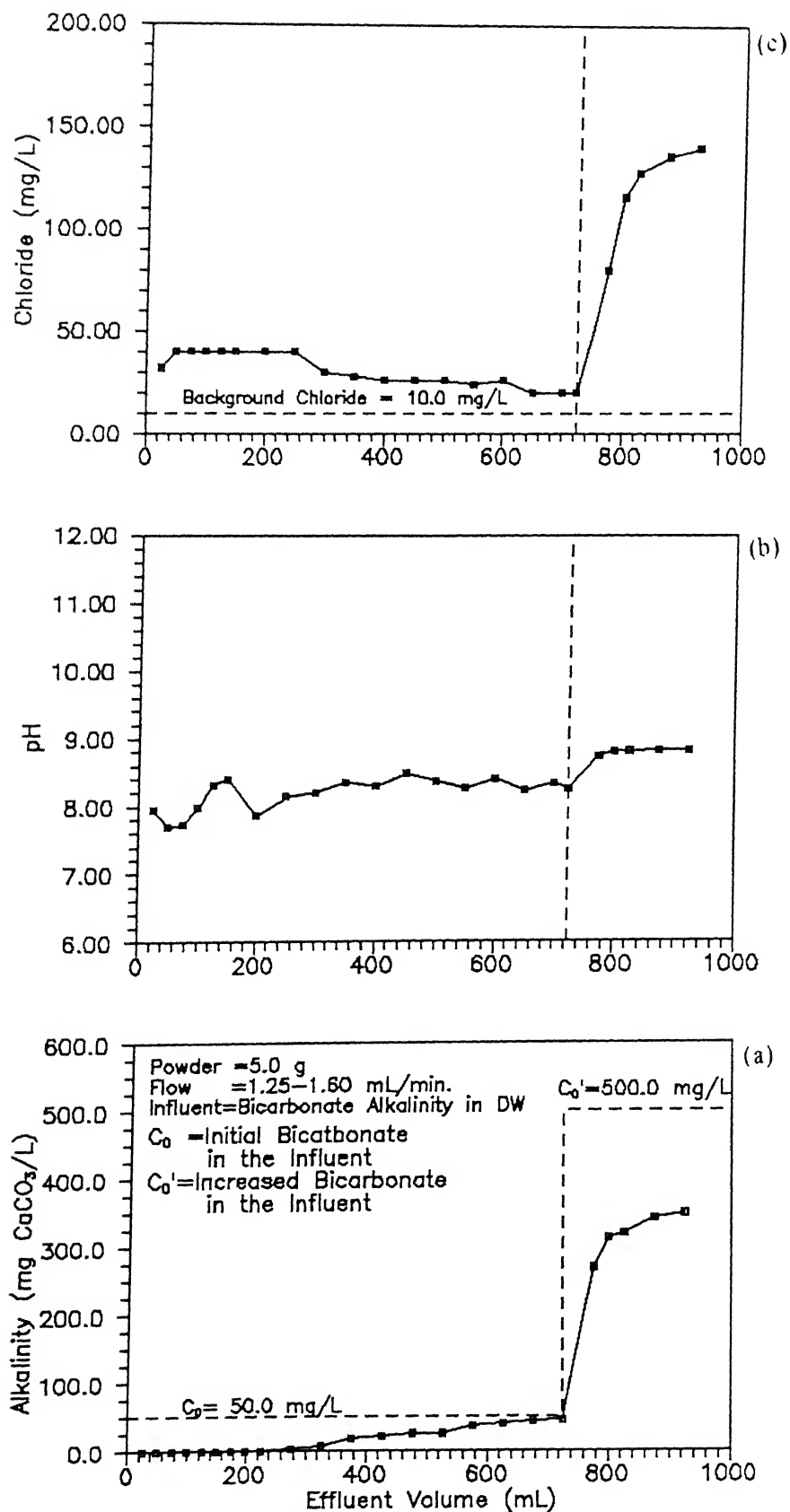
Fig. 5.32 Effect of Bicarbonate on HBO(2) Column Performance.
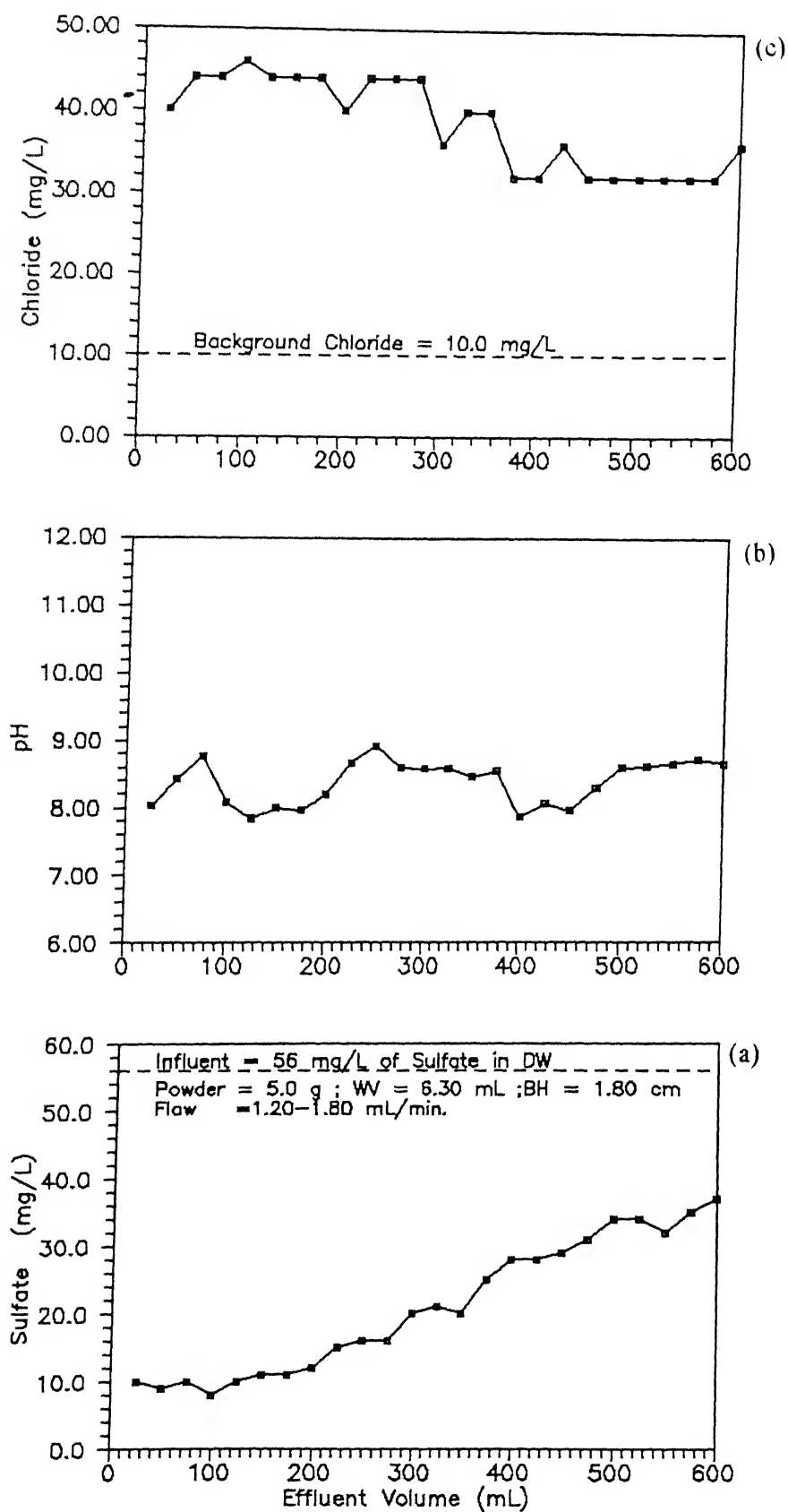
Fig. 5.33 Effect of Sulfate on HBO(2) Column Performance.

5.7 REMOVAL OF NITRATE IN PRESENCE OF COMPETITIVE ANIONS

Observations indicated that bicarbonate and sulfate are also sorbed on HBO (2) powder, and chloride exchange is the major mechanism of these sorption. Apart from them , depending on the concentration, chloride itself may affect the nitrate sorption behavior of the powder. Hence experiments were conducted to study the removal of nitrate in presence of these anions

5.7.1 Effect of Chloride

Although HBO powders indicate chloride exchange for nitrate sorption in distilled water systems , the level of chloride in the influent may affect the efficiency of nitrate removal. In order to study the effect of level of chloride on nitrate removal, the influent chloride was varied from 1 to 10 meq/L (35.5 to 355mg/L) and nitrate removal at 1 meq/L level in distilled water system by HBO (2) powder was monitered. The results are presented in Fig. 5.34. It is observed that the nitrate removal decresed almost linearly with increasing level of chloride in the influent. Monitoring of final level of chloride revealed that depending on the influent chloride concentration, the powder may also take up chloride from the solution. The results of a typical analysis is shown in Fig. 5.35. It indicates that as long as the chloride in the influent is below about 2.5 meq/L, at I meq/L nitrate level the net effect is an increase of chloride in the final solution. When the chloride in the influent increses beyond about 2.5 meq/L, there is a decrese in the chloride concentration in the final solution, indicating that HBO (2) column is possibly being regenerated by increased level of chloride.
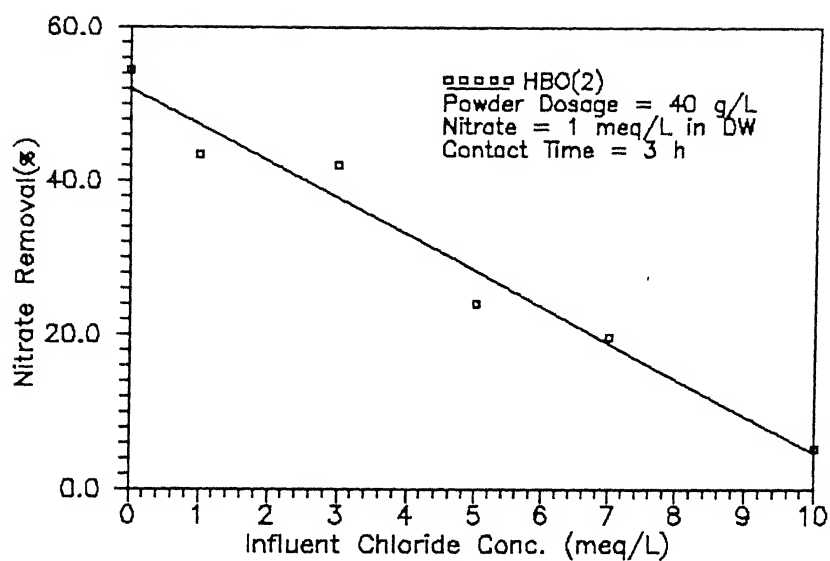
Fig. 5.34 Effect of Influent Chloride Concentration on Nitrate Removal.
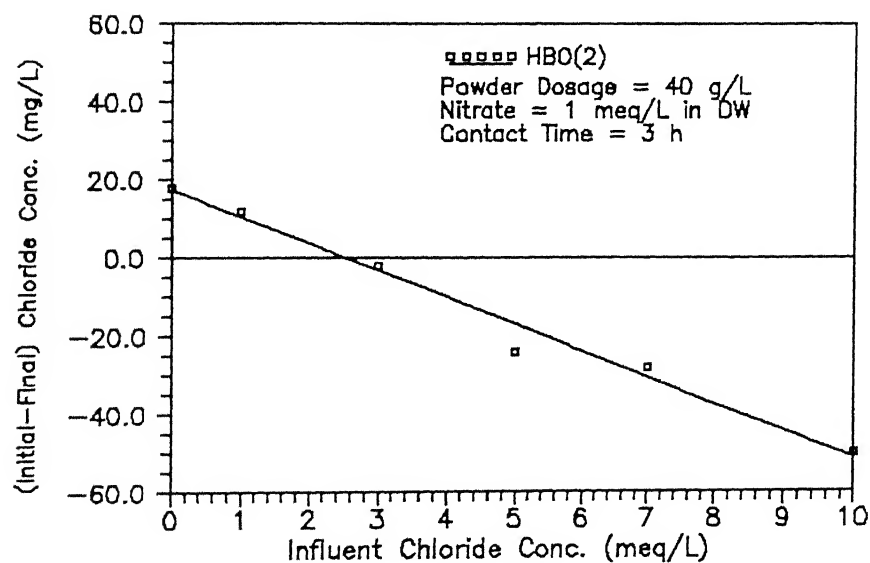
Fig. 5.35 Effect of Influent Chloride Concentration on Effluent Chloride Level.

5.7.2 Effect of Bicarbonate and Sulfate

Effect of presence of bicarbonate and sulfate on nitrate removal by the powder were studied using three parallel columns, each with 5.0g of HBO (2) The first column was fed with 1 meq/L nitrate; the second with 1 meq/L each of nitrate and bicarbonate, and third with 1 meq/L of nitrate with 1 meq/L of sulfate as influent. The effluents from the columns were analysed for the remaining nitrate concentration in them. The results are shown in Fig. 5.36. Even though the amount of powder in columns appeared insufficient resulting in quick near breakthrough, the trend of curves indicated that even at equal level (1 meq/L), alkalinity affects nitrate removal more adversely than sulfate. Thus, at 1 meq/L concentration levels of nitrate, bicarbonate, and sulfate HBO powders appear to follow a preference series of ions removal as:

$$HCO_3^- > SO_4^- > NO_3^-$$

5.8 PERFORMANCE OF HYDROUS BISMUTH OXIDES IN NITRATE REMOVAL FROM GROUND WATER

5.8.1 Column Run With 1 meq/L Nitrate in Ground Water

With a view to study the behaviour of HBO powders in ground water treatment application, a downflow column with 10.0 g of HBO (2) powder was run. I.I.T. Kanpur ground water added with 1 meq/L (= 14.0 mg N/L) of nitrate was applied as influent. Effluent samples were analysed for (residual) nitrate,
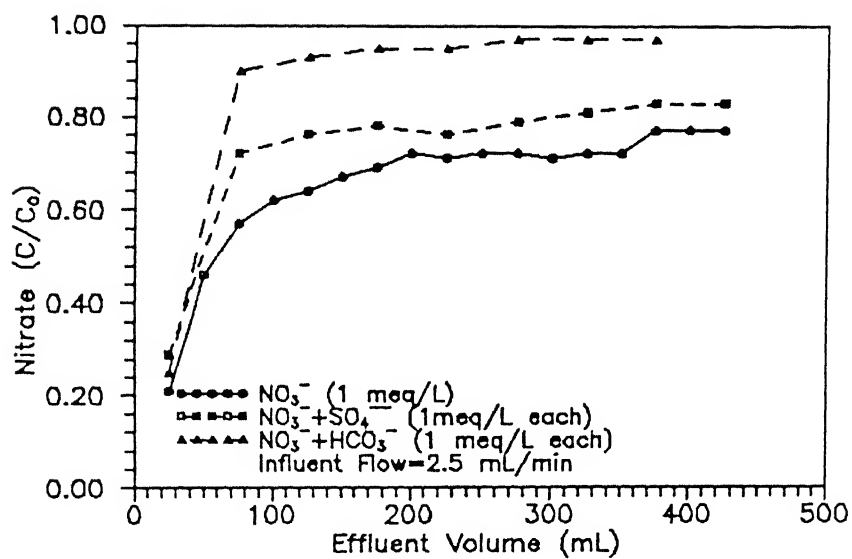
Fig. 5.36 Effect of Alkalinity and Sulfate on Nitrate Removal

in HBO(2) Column.

alkalinity, chloride, sulfate and pH. Fig. 5.37 (a) through (e), show the effluent quality from the column. From Fig. 5.37 (a), it appears that initially there is very small nitrate removal from water. However, similar to organic resins, the phenomena of "nitrate dumping" (Guter, 1991) was observed with HBO powder also. In strong base anoin exchange resins also, the bed removes nitrate from the flow in the beginning, but when competitive anions like bicarbonate or sulfate reach the site, they often displace the sorbed nitrate. Thus a sudden rise in nitrate concentration appears in the effluent. Because of a very low level of nitrate and relatively high concentration of bicarbonate in the influent, the sorption as well as "dumping" of nitrate by HBO (2) powder is small. Fig. 5.37 (b) reveals that there is an appreciable rise in pH of the effluent. It appears that due to very high level of bicarbonate in the influent (around 9.0 meq/L), hydroxyl ions are also affected in the medium. Figure 5.37 (c) and (d) show the residual alkalinity and sulfate in the effluent. It appears that significant portion of the alkalinity and sulfate are sorbed by the powder. The chloride concentration in effluent is quite variable, as shown in Fig. 5.37 (e). A sample computation of total anions removed and total chloride released in the effluent for a part of flow (between 450 to 750 mL volume) during the column run gave a chloride exchange ratio (CER) of 0.48. The elevated level of chloride in effluent, and reduction in bicarbonate (measured through alkalinity) and sulfate concentrations, in themselves point towards chloride exchange by the powder. As observed earlier, when the level of chloride in water increases above around 100 mg/L, the powder starts taking up chloride also from the water in

Fig. 5.37 Effluent Quality from HBO(2) Column
with 1 meq/L Nitrate Spiked Ground Water.
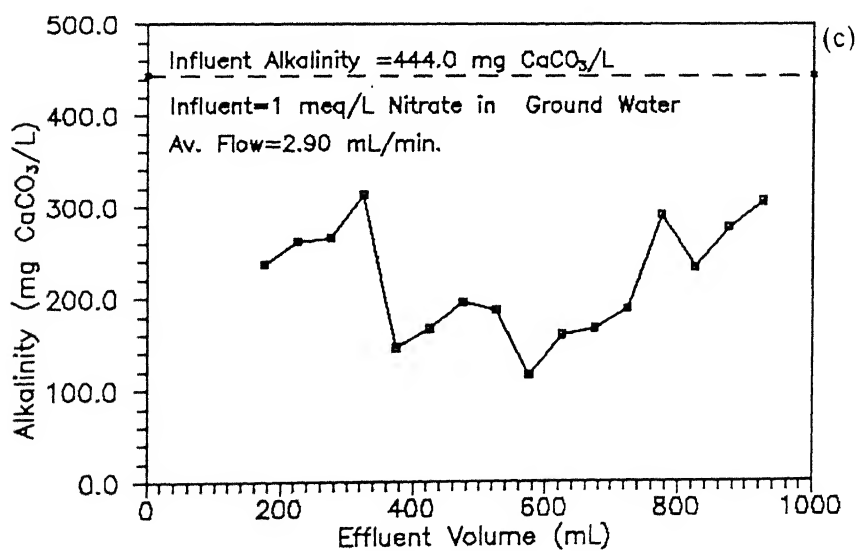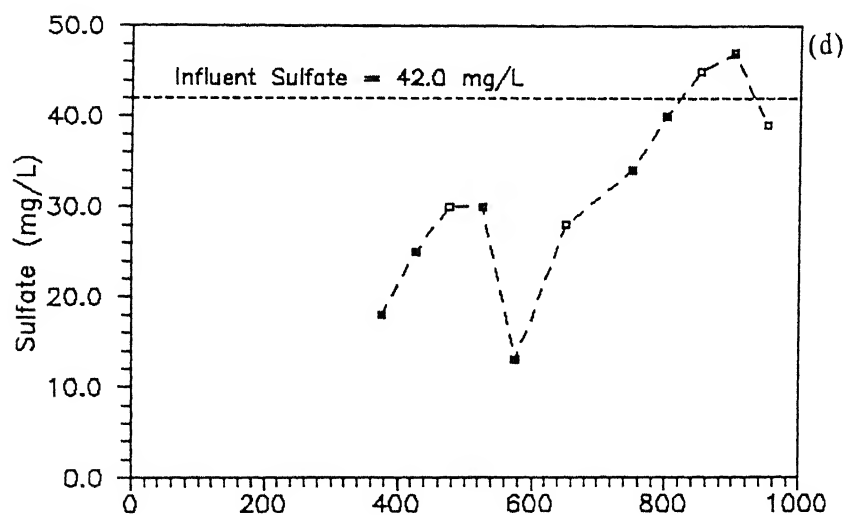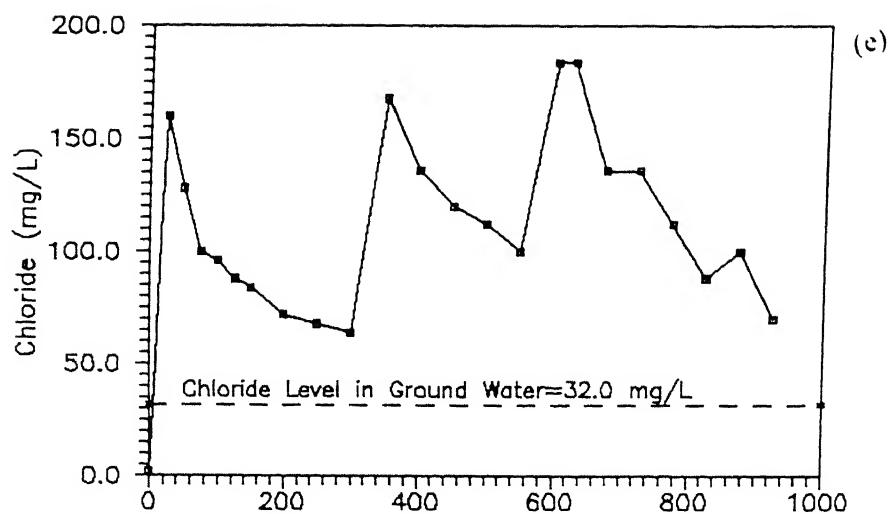
Fig. 5.37 Continued....

contact. Between 450-750 mL effluent volume, the average chloride level is around 140.0 mg/L, which is the resultant concentration after all interactions between the medium and the ions present in the aquous environment around. This may partly explain a comparatively lower CER value observed in sample computation. From Fig.5 37 (d), a "sulfate dumping" from the column is also observed. The bicarbonate (alkalinity) continues to be getting sorbed. as shown in Fig 5 37 (c) Ths implies that bicarbonate ions are gradually replacing the sorbed sulfate in the medium.

5.8.2 Column Run with 2 meq/L Nitrate in Ground Water

Experiments with 1 meq/L nitrate in ground water revealed a phenomena of "nitrate dumping" in effluent. The phenomena of "nitrate dumping" in retrospect indicated some initial uptake of nitrate from water by the powder. In order to further observe this phenomenon, performance of a column with 2 meq/L of nitrate in ground water as influent was monitored. Fig. 5.38, (a) through (e), shows effluent quality from this column. In this case, the behaviour of "nitrate dumping" was more pronounced, as shown in Fig. 5.38 (a). Subsequently however, the nitrate level in effluent remained consistently below the influent level in this experiment. From Fig. 5.38 (c) and (d), it is observed that the effluent shows "sulfate dumping" when alkalinity remains getting sorbed. This may be due to a combined effect of high concentration as well as high preference for bicorbonate in HBO (2).
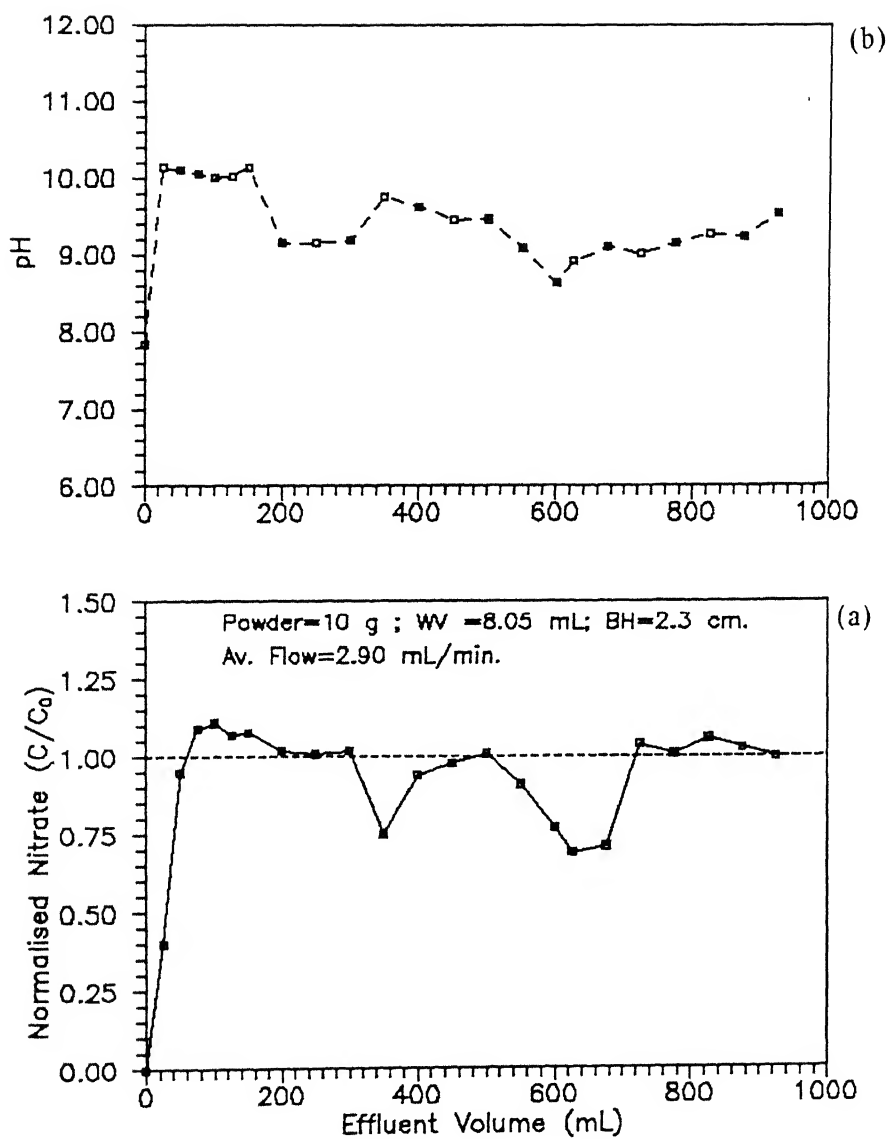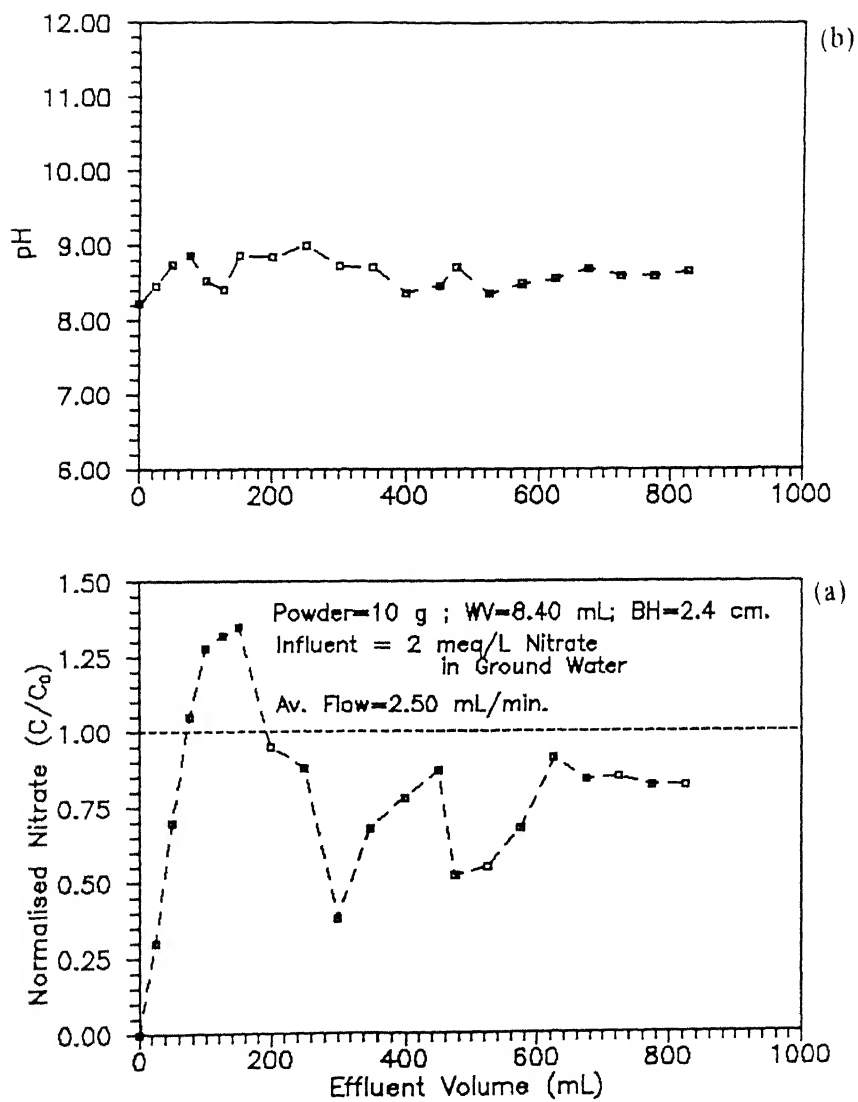
Fig. 5.38 Effluent Quality from HBO(2) Column
with 2 meq/L Nitrate Spiked Ground Water.

(e)

Chloride Level in Ground Water=32.0 mg/L

(d)

Influent Sulfate = 42.0 mg/L

(c)

Influent Alkalinity =444.0 mg CaCO₃/L

Influent = 2 meq/L Nitrate in Ground Water

Av. Flow=2.50 mL/min.
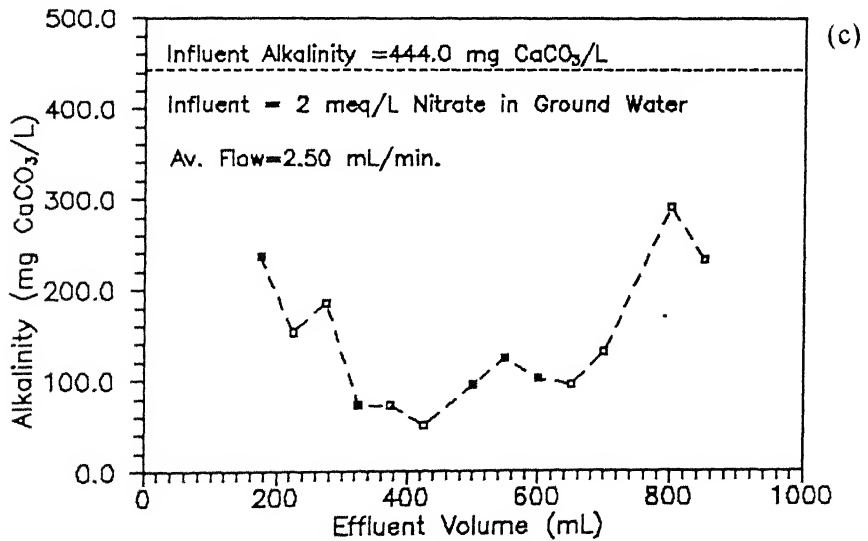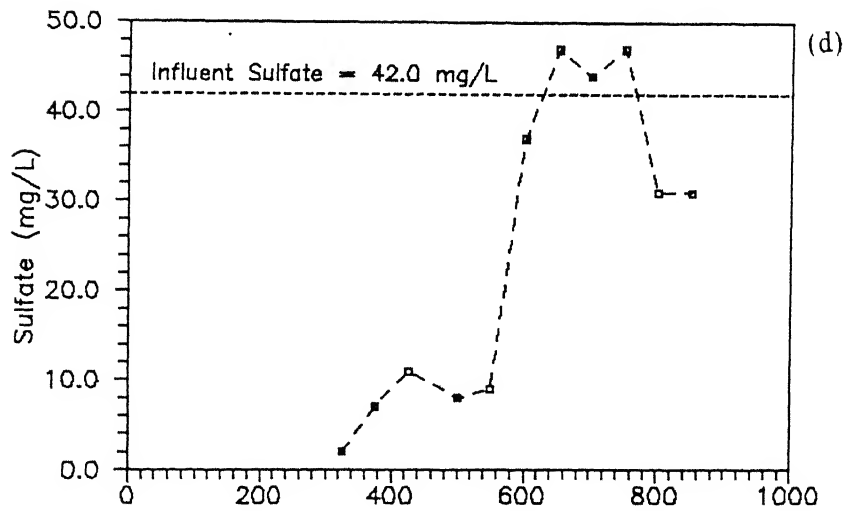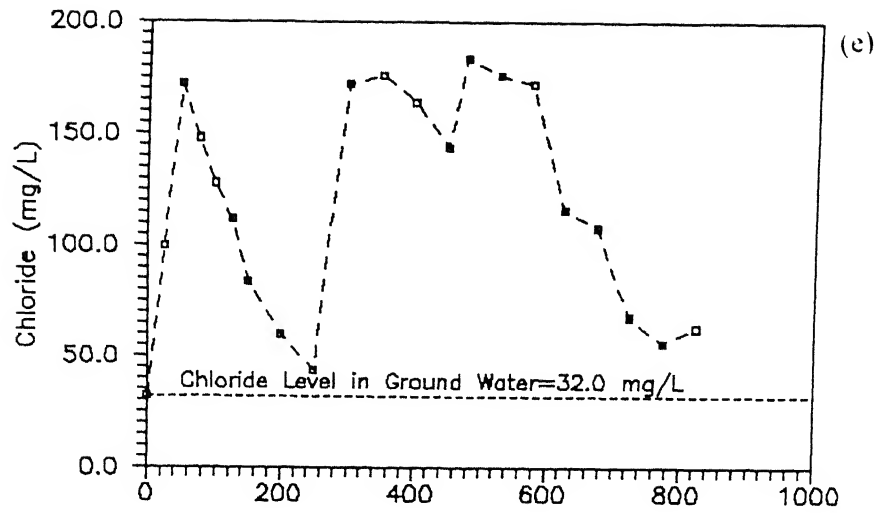
5.8.3 Regeneration of Column

The column run with 2 meq/L nitrate in ground water was regenerated using 0.1N NaCl solution. The effluent samples. collected in 10 mL volumes during regeneration, were analysed for nitrate. chloride. alkalinity and sulfate The results indicated a small amount of nitrate being eluted from the medium As shown in Fig. 5.39, the alkalinity in the regenerant effluent initially increased and then followed a decreasing trend, indicating gradual elution of sorbed alkalinity. The sulfate concentration displayed a similar trend. but quicker elution than the bicarbonate alkalinity. Thus, bicarbonate appears to be a major cause of concern for nitrate removal from ground water using these media. Hence some pretreatment of water for bicarbonate alkalinity reduction is necessary before an effective use of hydrous bismuth oxide in nitrate removal from ground water.
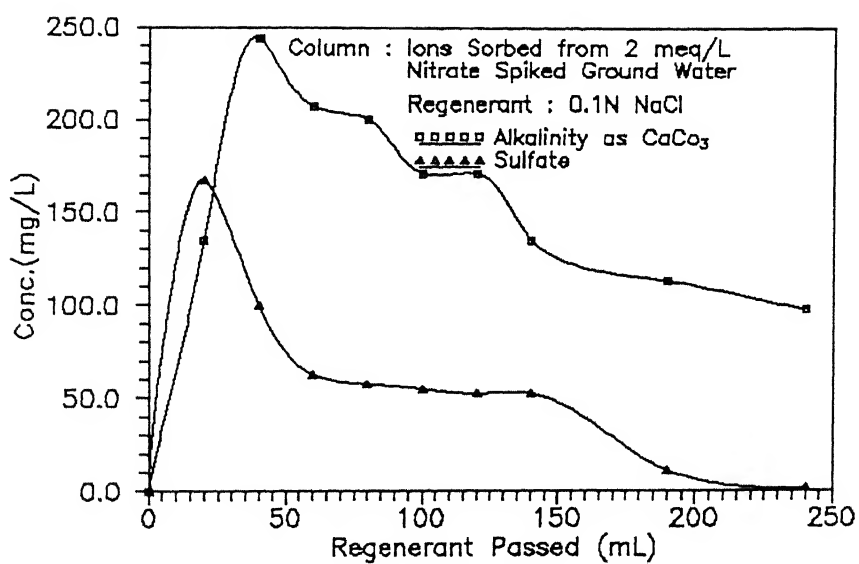
Fig. 5.39 Elution of Sorbed Alkalinity and Sulfate

from HBO(2) Column.

CHAPTER 6

SUMMARY AND CONCLUSIONS

6.1 SUMMARY AND CONCLUSIONS

With a view to develop an inorganic medium for nitrate removal in drinking water purification, bismuth compounds in the form of oxide, oxychlorides, carbonate and hydroxide were subjected to short duration batch screening tests to assess their potentials and identify the most promising compound. These tests indicated that bismuth hydroxide in its yellow colored composition gives best performance in terms of nitrate removal. Preparative conditions of hydrous bismuth oxide (HBO) affect the physicochemical properties of the product significantly. Three HBOs, designated as HBO (1), HBO (2) and HBO (3) were prepared from mixing a 0.1M Bi_2O_3 solution in 2N HCl and increasing volumetric proportions of 1:1, 1:2 and 1:3 of 2N NaOH respectively. Out of the three HBOs, HBO (1) is white in color, but HBO (2) and HBO (3) are predominantly yellow. At 1 meq/L nitrate level with a powder dosage of 40 g/L and a contact time of 24h, HBO (1) shows a removal of 16%, but for HBO (2) and HBO (3) it is 81.6 and 81.7% respectively. Initial pH of solutions within 3 to 9 range did not affect the nitrate removal by yellow bismuth hydroxide significantly. Specific gravity for HBO (1), HBO (2) and HBO (3) were determined as 5.80 ± 0.1, 7.0 ± 0.08, and 6.9 ± 0.10 respectively. pH_{pzc} for Bi_2O_3, HBO (1), HBO (2) and HBO (3) were estimated to lie between 8.0-8.2, 6.5-6.7, 9.7-10.3, and 9.3-9.7 respectively. Investigations revealed that HBO (1), HBO (2) and HBO (3) had a chloride

Tests to study the effect of other competitive ions such as bicarbonate and sulfate indicated decrease in nitrate removal in presence of these ions HBO (2) showed Preference of ion sorption as

$$HCO_3^- > SO_4^{--} > NO_3^-.$$

Tests for nitrate removal from 1 and 2 meq/L nitrate spiked ground water indicated that similar to organic ion exchange resins, HBO (2) also showed nitrate (and sulfate) "dumping", suggesting preferential sorption of bicarbonate alkalinity. Hence a pretreatment of ground and surface waters for decreasing the levels of alkalinity and sulfate appears desirable before removal of nitrate using bismuth based media in water treatment applications.

6.2 SUGGESTIONS FOR FURTHER WORK

(1)   Mode of existence of chloride in the hydrous bismuth oxide precipitates may further be investigated to understand the formation and controlling properties of HBOs in ion exchange use.

(2)   Instead of drying by application of heat, other techniques of precipitate dehydration and their effects on nitrate removal may be studied.

(3)   Granulation of HBO particles or coating of precipitate over some inert material may be investigated in order to make the media more useful in home water filter applications.

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APPENDIX I

Physico chemical Properties of Common Bismuth Compounds

SL No	Compounds	Formula Weight	Color and Crystallinity	Density
1	(a) Bi_2O_3	466 00	Yellow, Rhombic	8 90
	(b) Bi_2O_3	466 00	Yellow, Tetragonal	8 55
	(c) Bi_2O_3	466 00	Yellow, Cubic	8 20
	(d) $Bi_2O_4.2H_2O$	518 03	Brown Yellow	5 60
	(e) Bi_2O_5	498 00	Brown	5 10
	(f) $Bi_2O_5 H_2O$	516.02	Red	5 75
2.	(a) $Bi(OH)_3$	260.02	White, Amorphous	4 36
	(b) $BiOOH$	242 00	Yellow	-----
3	$BiOCl$	260 46	White	7 72
4	$(BiO)_2CO_3. H_2O$	528.03	White	6.86
5	$BiONO_3. H_2O$	305 02	Hexagonal Plates	4 93

* Source. Bhatki (1977); Muylder and Pourbaix (1966); Gmelins (1964).

APPENDIX II

ΔG^0_{298} Values of Selected Bismuth Compounds.

Compounds	ΔG^0_{298} (Kcal/moles)	References
Bi_2O_3 (c)	-118.55	Gmelins, (1964)
$Bi(OH)_3$ (c)	-138.55	Gmelins, (1964)
$BiOOH$ (c)	-88 4	Gmelins, (1964)
$Bi(OH)_2Cl$ (c)	-128 71	Wagman et al., (1965)
$BiOCl$ (c)	-77 0	Wagman et al., (1965)
$BiONO_3$ (c)	-67 0	Wagman et al., (1965)

ERRATUM

Page	Line	Existing	Should Read
8	16	cynosis	cyanosis
18	1	32.6	22.6
21	1	$2Al + OH)_3$	$2Al(OH)_3$
22	10, 15	Tacke et al.	Tacke and Vorlop
26	13	1.0 mg	0.1 mg
29	20	Italey	Italy
31	12	anthecite	anthracite
34	13	0 35 mg/L	0.35 mg
34	14	1.0 mg NO_3^-	1.0 mg N
36	20	nitrate < 0.01 mg N/L.	nitrite < 0.01 mg N/L.
39	2	quaternuary	quaternary
42	5	Wenli et al.	Wenli and Hua
49	21	antisceptics	antiseptics
49	21	Sadler (1991)	Salder (1991)
50	Table 2.2	Admddission $B(NO_3)_3$	Admission $Bi (NO_3)_3$
53	3	compunds	compounds
53	7	Anand and Baxi: 1978;	Anand and Baxi, 1978a;
54	15	sccale	scale
58	13	KOH	NaOH
59	12	KOH	NaOH
64	6, 7	Anand and Baxi (1978)	Anand and Baxi (1978a)
66	1, 2	Krause et al. (1935)	Krause (1935)
66	19	...Nirate..	..Nitrate..
72	15	..Helffrich`s..	..Helfferich`s..
76	2	..Helffrich`s..	..Helfferich`s..
78	4	efflent	effluent
100	11	coloumns	columns
102	10	Table summarises	Table 5.2 summarises
103	21	(missing)	WV = Wet Volume; BH = Bed Height
104	3	Table summarises	Table 5.3 summarises
104	8	1.4 and 1.3	1.47 and 1.26
104	9	mg/L	mg N/g
106	21	Figure 5.23 and 5.24 appear on page 109	Figure 5.23 and 5.24 should appear on page 108
119	14, 20	decresed, decrese	Decreased, decrease
123	4	(Guter, 1991)	(Guter, 1995)
135	1, 2	Braester, C. and .. 149-163.	Deleted
135	17	Clifford, D., and	Clifford, D.A. and
135	19	Clifford, D., and	Clifford, D A. and
135	24	Clifford and	Clifford, D.A. and..
135	26	Hydrogentrophic	Hydrogenotrophic
137	1	N-nitrso	N-nitroso
140	3	(1993)	(1993a)
140	6	(1993)	(1993b)
140	9	Methogenesis	Methanogenesis
140	19, 20	Mateju, V., Cizinska, ...86-90	Deleted
141	24, 26	Pawar, N.J., and.. ..197-204.	Deleted
141	23	Roennefaht	Roennefahrt
143	28, 29	Singh, B.K., Pal,.. ... 46-49.	Deleted
143	30	Soars	Soares
145	1	Wadia, D.N. (1960) ...1-58.	Deleted